THE SYNTHESIS AND N.M.R. SPECTRA OF SOME DIFLUOROPHOSPHINO-NITROGEN COMPOUNDS

by

John Gillespie Wright

A thesis presented for the degree of
Doctor of Philosophy in the Faculty of Science
of the University of Edinburgh, 1980.

Contents

Acknowledgements

"I get by with a little help from my friends"

J. Lennon and P. McCartney.

I would like to thank various people for help of many different kinds, starting with my supervisors Professor E.A.V. Ebsworth and Dr. D.W.H. Rankin - for suggesting the initial line of work, for giving me complete freedom to indulge in any area of research which attracted my attention, for useful suggestions and positive criticisms.

I thank all my colleagues past and present for general practical advice and stimulating discussions, in particular Dr. A. Robertson and Dr. D.E.J. Arnold for initiating me into the mysterious world of vacuum lines and PF_2 chemistry. Dr. S. Cradock kindly ran the photo-electron spectra and often assisted in their interpretation, while Steve Henderson taught me basic glassblowing and repaired some of the glassware I damaged. I am obliged to Dr. Alan Boyd for the care he took to produce good n.m.r. spectra from my samples.

I thank Mrs. M. Manson for the mammoth task of typing the manuscript.

I am indebted to Alison and Lorna Leslie and Dr. Mary Mercer for consistently nagging at me to finish writing this thesis, for their weird senses of humour, and for other things.

However, without a doubt I owe a great deal to one person in particular. For making me think of applying to Edinburgh University, for putting up with my fits of depression, for continual encouragement, for thinking I was clever (?), for ensuring I wrote my thesis, for help in every way, for asking me to marry her,
ta, Carole, ta much.

Summary

The following new compounds have been synthesised via reaction S:1 - $PF_2[NH(R')]$ (R' = $SiMe_3$, GeH_3) and $PF_2[NR(R')]$ (R = GeH_3, SiH_3, PF_2; R' = GeH_3, SiH_3).

$$PF_2(NH_2) \text{ or } PF_2[NH(R)] + R'X + NMe_3 \rightarrow PF_2[NH(R')] \text{ or } PF_2[NR(R')] + [NHMe_3]^+X^- \quad \ldots\ldots \text{S:1}$$

Reacting PF_5 with $PF_2[NH(SiH_3)]$ gave $NH(PF_2)(PF_4)$; similarly reacting PF_2Br with $SiH_3(NC_4H_4)$, and with BSA, yield novel $PF_2N<$ species, as did reacting PF_2Br and NMe_3 with HNC_4H_4, and with $CH_3CO.NH_2$. Oxidative addition of NH_3 to PF_2H produced $PF_2H_2(NH_2)$, while some halogen exchange reactions of $PF_2(NMe_2)$, and the reaction of N_2H_4 with PF_2Br, were studied briefly. Reactions of some of these compounds with HX, S, H_2O and B_2H_6 were studied, the latter forming new $H_3B.P<$ adducts with $PF_2[N(SiH_3)_2]$, $PF_2[NC_4H_4]$ and $N(PF_2)_2(SiH_3)$ (1:1 and 2:1).

All these compounds were characterised by ^1H, ^{19}F and ^{31}P n.m.r., and, where practical, by i.r., Raman, mass and P.E. spectroscopy. The orientation of all the PF_2 groups is strongly influenced by F--H interactions, resulting in two conformers being present in gaseous $PF_2[NH(SiMe_3)]$ and $PF_2[NH(GeH_3)]$, as shown by two N--H stretches in the i.r. spectra. The stability of several of the compounds seemed to be enchanced by F--H interactions.

The following coupling constants, J_{PX}, were found to be large when X was cis to the P^{III}'s lone pair, and small when trans to the lone pair, especially at low temperatures:- $^{2}J_{PNH}$, $^{2}J(P^{29}Si)$, $^{2}J_{PNP}$, $^{3}J_{PNSiH}$, $^{3}J_{PNGeH}$, $^{3}J_{PNPF}$, and $^{4}J_{PNCCH}$. Fast rotation about the P-N bond at room temperature often averaged the two extreme values of J_{PX}. In the BH_3 adducts, where there is no lone pair, J_{PX} was similar to the value observed when X was trans to the lone pair. A Karplus-type relationship of $^{3}J_{FPNH}$ versus $\angle$ FPNH is also suggested, while $^{2}J(FP^{15}N)$ is large when the fluorine can hydrogen-bond, i.e. is cis, to an amino proton; F--H interactions may also result in some J_{FH}'s and $^{3}J(^{29}SiNPF)$ being larger. The signs of the various couplings in $PF_2[^{15}N(MH_3)_2]$ (M = Si, Ge) were found by double resonance, while some of the signs in $NH(PF_2)(PF_4)$ and $N(MH_3)(PF_2)_2$ (M = Si, Ge) were determined by spectral analysis.

FOR CAROLE.
FOR LOVE IS
FOR EVER.

XII

"We know your idea's crazy,

but is it crazy enough?"

—Niels Bohr

Chapter 1

Historical Background and Introduction

"Ohne Phosphor kein Gedanke" anon.

The history of phosphorus chemistry stretches far back into antiquity, into the earliest realms of alchemy. The element was probably known to the old Arabian alchemists, especially Alchid Bechil[1] in the 12th century, for he and people like Abu Bakr Muhammed[2] and the compounded character Abu Musa Jabir[2] were for ever distilling urine, bones, excrement and other phosphatic materials under conditions where phosphorus was sure to have been produced.

However isolation of the element is generally accredited to Hennig Brandt[3], an impoverished merchant and alchemist who, in 1669, in trying to recover his lost wealth by converting base metals into gold, took a large quantity of partially digested urine and distilled off the volatiles till the remaining liquor resembled thick syrup. After adding sand, and still further distillations he succeeded in condensing phosphorus, in a cooled container, over water.

The name phosphorus - from the Greek φως, light, and φερω, I bear - was originally given to all phosphorescent substances before being restricted to the element, which originally bore names such as phosphorus mirabilis or noctiluca consistens.

After its discovery, phosphorus chemistry progressed rapidly and by about 1770 phosphorus was recognised in bones and teeth[4], and by 1850 the significance of phosphates as fertilizers was also known[5].

Even from its earliest beginnings, many famous chemists have been associated with phosphorus chemistry. By 1811, the discovery of the halides, PCl_3, PCl_5 and perhaps PF_3 as well, was made in France by Gay Lussac and Thenard[6], and in Britain by Davy[7], and the ensuing investigation of the reactive nature of these compounds is related in Mellor's Treatise[8]. These discoveries were soon followed by the emergence of phosphorus-nitrogen chemistry - Davy[7] said that PCl_5 formed a definite compound with NH_3, in 1810; in 1834 Rose[9] claimed a complex of the formula $PCl_3.5NH_3$ on heating gave $HNPNH_2$ and NH_4Cl; Liebig[10] made, in 1834, what was later shown to be $(PNCl_2)_n$ in 1846 by Gerhart[11] who also synthesised $PCl_3(NH_2)_2$. An extensive review by Michaelis[12] on the work of his students on P-N chemistry appeared in 1903. This described the synthesis of several series of compounds of the general formula $(RR'N)_nP(X)Cl_{3-n}$ (where R = alkyl, aryl; R' = alkyl, aryl, or H; X = lone pair, O, S; n = 1, 2, 3). For example, the reaction of PCl_3 with secondary amines gave, depending on the ratio of the reactants, $PCl_2[NRR']$, $PCl(NRR')_2$ or $P(NRR')_3$; primary amines and PCl_3O gave $PCl_2[NHR](O)$, $(OPCl_2)_2NR$, $OPCl(NHR)_2$, etc. But although compounds such as $PCl_2[NH(C_2H_5)]$ and $PCl_2[N(CH_3)_2](S)$ were known from the beginning of the 20th century, work on the equivalent fluorides was somewhat neglected.

The nature of the fluorides of phosphorus was not clear until the advent of H. Moissan's classic studies on fluorine, when he prepared[13] the parent fluorophosphine, PF_3, as early as 1884 - like Brandt this was not the intended product, but unlike Brandt he eventually achieved his goal, the isolation of fluorine[14]. In 1877 PF_5 was discovered by Thorpe[15] who also claimed the synthesis of $PF_5.5NH_3$, while Poulenc[16] reported $PF_3(NH_2)_2$ in 1891.

But apart from a few sporadic reports such as work on chloro- and bromofluorophosphines[17,18], interest was not revived in this field until the late 1950's, and the 1960's may be described as the real renaissance of fluorophosphine chemistry.

The first literature report of $PF_2(NMe_2)$ appeared in 1962[19] - 59 years after that[12] of $PCl_2(NEt_2)$ - the preparation being described in M.A. Fleming's Ph.D. thesis[20] in 1963 and also by Noeth and Vetter[21] in 1963. There are several synthetic routes to this compound. Reaction of PF_3 with $HNMe_2$ yields[22] $PF_2(NMe_2)$ and $PF(NMe_2)_2$, as does[23] PF_3 and $P(NMe_2)_3$. Similarly[21] BF_3 and $P(NMe_2)_3$ gives $PF_2(NMe_2)$, but the usual synthesis[24] is the fluorination of $PCl_2(NMe_2)$ with SbF_3 or NaF in an inert solvent. Primary amines and PF_3 yield[25] $PF_2(NHR)$, $PF(NHR)_2$ and $PF_2H(NHR)_2$ (R = Me, Et, Bu^n, Bu^t). The early patent literature[26] describes the fluorination of $PCl_2(NEt_2)$ by SbF_3 to give $PF_2(NEt_2)$, but the physical properties quoted are distinctly different from those obtained by Schmutzler[24] on an authentic sample from a similar synthesis in 1964.

From this time on, the literature has expanded steadily on all fronts, with the main research concentrated on

phosphoramidous fluorides, alkyl- and arylfluorophosphines, fluorophosphites, the aforementioned halogenofluorophosphines, and the wide area of fluorophosphine - co-ordination complexes - another accidental discovery of Moissan's[27].

Several useful reviews have been published due to the increased interest in this field. General phosphorus fluorides were covered by Schmutzler[28] in 1965. Transition metal complexes were reviewed[29] by Kruck and halogeno- and pseudohalogenophosphines by Schmutzler and Fild[30]. A wide ranging useful review of developments in fluorophosphine chemistry up to 1970 has been published by Nixon[31].

And yet, despite the considerable number of dialkyl- and diarylaminodifluorophosphines which were reported, and the formation of the $PF_2(NHR)$ series of compounds, the simplest member of the series, $PF_2(NH_2)$, was not synthesised until 1970, by Rankin[32], and Cohn[33]. It was 1967 before Nixon[34] prepared the $N(PCl_2)_2R$ and $N(PF_2)_2R$ series of compounds, and in 1975 Arnold[35] isolated $NH(PF_2)_2$ and $N(PF_2)_3$. The success of the latter work depended on the ability of NMe_3 to abstract HX (X = Cl, Br, I) from mixtures of $PF_2(NH_2)$ and PF_2X, thus overcoming the reduced basicity of $PF_2(NH_2)$ compared with NH_3, (reactions 1:1, 1:2).

$$PF_2Br + 2NH_3 \rightarrow PF_2(NH_2) + NH_4Br \qquad 1:1$$

$$PF_2(NH_2) + PF_2Cl + NMe_3 \rightarrow NH(PF_2)_2 + N(PF_2)_3 + [NHMe]Cl \qquad 1:2$$

(unbalanced)

With only two exceptions, however, all the known $PF_2(NR_2)$, $PF_2(NHR)$, and $N(PF_2)_2R$ derivatives were based on the first member of Group VI, carbon. The exceptions were $PF_2[NH(SiH_3)]$[36] and $PF_2[NMe(SiMe_3)]$[37].

Silicon-nitrogen compounds were first prepared 150 years ago[38], but the relevant compounds for this work, $N(SiH_3)_3$ and $NH(SiH_3)_2$, were first synthesised[39] by the early pioneers of vacuum-line work, Stock and Somieski, in 1921, from SiH_3Cl and NH_3. Although $N(SiH_3)_3$ is reasonably stable, $NH(SiH_3)_2$ is somewhat unstable and the existence of $NH_2(SiH_3)$ is doubtful.

Trisilylamine is only weakly basic, and its structure has been shown to have a planar NSi_3 skeleton[40,41]. Both of these properties have been attributed to $p\pi \rightarrow d\pi$ bonding[41,42,43,44], in which the nitrogen's lone pair is donated to the silicon's empty 3d orbitals. As a result of the interest generated in either proving or disproving this hypothesis, quite a variety of silyl amines have been prepared, with groups other than H or SiH_3 on the nitrogen, and their chemistry well investigated and reviewed[43].

Apart from being stabler than might be expected (cf. $NH(SiH_3)_2$), the structure of $PF_2[NH(SiH_3)]$ is also unusual. As well as having a planar nitrogen, it was shown[36] by i.r. and e.d. studies that two conformers were present in the gas phase, due to two favourable orientations in which the PF_2 group can interact with the amino and silyl protons. The main intention of this work was to extend the number of $PF_2N\langle$ compounds where F--H interactions made an important contribution to the structure(s) the molecule adopted, and to extend the number of $PF_2(NRR')$ derivatives where R and R' were not alkyl or aryl groups. To this end recourse would have to be made to GeH_3 as well as SiH_3 derivatives.

Unfortunately germyl amine chemistry is nowhere near as fruitful a research topic as the silyl amines - only $N(GeH_3)_3$ has ever been prepared and isolated, and the situation is best summed up by some quotes from Rankin's paper[45] on the above

compound - "... the lifetime of a (gaseous) sample being ... ca. 1 minute, ... the liquid phase is considerably less stable, ... on no occasion has the solid amine been successfully revolatilised ...". But perhaps this stability problem might be overcome, due to the previously mentioned stabilising effect of a PF_2 group in $PF_2[NH(SiH_3)]$.

One useful property of Si-N bonds is the ease with which they may be cleaved by R_nMX halides the R_nM-group usually replacing the SiH_3 or $SiMe_3$ originally bound to the nitrogen. This useful and widely applicable synthetic route has been reviewed by Fessenden and Fessenden[43], and Scherer[46]. It was proposed that whenever it was relevant, such cleavage reactions would be investigated as an extension of Arnold's work[47] on such systems.

The existence of the $N(PF_2)_2R$ and $N(PCl_2)_2R$ series of compounds has already been alluded to, but a P-N-P linkage need not be confined to just two P^{III} nuclei. A few chloro- and fluoro-substituted P^VNP^V derivatives are also known. Lustig[48] synthesised $PF_2(NPF_3)(E)$ (E = O,S) while Glemser[49] reported $PF_2(NPF_3)(O)$. Charlton and Cavell[50] made the compounds $X(PF_2E)_2$ (E = O,S, and X = O,S,NMe) although their attempts at producing $NH(PF_2E)_2$ only led to the formation of these compounds NMe_3 adducts.

More interesting are compounds where the two phosphorus nuclei are in different valence states linked by a bridge. A few examples are known where the P^V nuclei is four co-ordinate. Keat[51] made $NMe(PCl_2)(PCl_2E)$ (E = O,S), Lustig and co-workers[52] have prepared $PF_2(NPF_3)$ from $PF_2(NH_2)$ and PF_3Cl_2, while Charlton and Cavell[53], and Des Marteau[54] have prepared $E(PF_2)(PF_2E)$ (E = O,S). Finally, Sharp and co-workers[55] have isolated $NMe(PF_2)(PF_2O)$, and also $NMe(PF_2)(PF_4)$, the only mixed valence example containing a five co-ordinate

phosphorus. The synthesis of the simplest fluorinated $P^{III}NP^{V}$ compound, $NH(PF_2)(PF_4)$, was therefore considered to be worth attempting, the most convenient route being by cleaving the Si-N bond of $PF_2[NH(SiH_3)]$ with PF_5. Coincidently, this turns out to be very similar to Sharp's synthesis of $NMe(PF_2)(PF_4)$ from $PF_2[NMe(SiMe_3)]$ and PF_5, although we were not aware of this at the time.

As a few of the possible organic derivatives of $PF_2[NR^1R^2]$ had been neglected, these areas too would be investigated, specifically PF_2 derivatives of aromatic heterocycles and of amides were non existent but considered to be accessible.

The compounds under investigation are all volatile liquids, have a rather revolting odour, and several of them are spontaneously explosive on contact with air or water. The toxicity of all P-F compounds is also a serious problem. Their relationship to nerve gases[56] such as Sarin, $PF(CH_3)(OC_3H_7)(O)$, should be born in mind, especially since $PF_2(NEt_2)(O)$ was once used as an insecticide[26] - fluorophosphine insecticides are sometimes described as nerve gases which simply work even better on insects than on man. These problems can be overcome by using a vacuum line for all synthetic procedures, and sealed n.m.r. tubes would allow samples to be handled conveniently while spectra are recorded.

N.m.r. spectroscopy has progressed greatly since its humble origin in 1945 when, independently, two physicists, Bloch[57], and Purcell[58], first observed the phenomenon. With the discovery of the chemical shift and its dependence upon the nuclear chemical environment (initially observed by Knight[59] in metals and metal salts in 1949, and then by Proctor[60] in nitrogen compounds and

Dickinson[61] in ^{19}F compounds) its usefulness to chemistry as a means of determining the basic structure or identity of a molecule was soon apparent.

Although initially mainly used to study protons, other nuclei soon emerged as equally important areas of study e.g. ^{11}B, ^{13}C, ^{19}F, ^{31}P. For the fluorophosphine chemist, n.m.r. has proved to be very useful due to the 100% natural abundance of ^{31}P and ^{19}F with $I=\frac{1}{2}$. The insensitivity of ^{31}P however meant that its full exploitation had to await the widespread availability of the Fourier transform n.m.r. spectrometer. The chemical shifts of a variety of types of phosphorus compounds have been found to occupy quite different areas[62], variations in valency, co-ordination number, and substituents being quite significant.

Coupling constants were first reported[63] in 1951 and when it was realised[64] how general an occurrence they were, the structural dependence of some couplings was investigated. Important factors include the oxidation state or the co-ordination number of the two nuclei coupled, or of any intervening nuclei, as well as the number of intervening bonds and the substituents on the nuclei concerned.

Since 1959, when Karplus[65] first formulated his ideas on the angular dependence of $^{3}J_{HCCH}$, $^{3}J_{HCCF}$ and $^{3}J_{FCCF}$ in ethane derivatives, several studies have related coupling constants to the molecular geometry and a large number of correlations of interproton couplings with structure have been reviewed by Sternhell[66]. It is found that $^{3}J_{HH}$ is large when the protons are trans to each other and small when they are cis; similar relationships[67,68] have been found for $^{3}J_{HF}$ and $^{3}J_{FF}$. This allows predictions of the molecular orientation to be made from a very

simple measurement. Another useful geometrical variation of J is that generally[69] in a whole host of phosphorus ligand-transition metal complexes $^{2}J_{PMP}$ is small if the ligands are cis and large if they are trans.

It has also been noted that if the number of intervening bonds is large but the two nuclei are close together in space, then larger than usual values of J are sometimes found[67,70]. Although termed through space couplings, they occur due to electronic interactions such as hydrogen bonding.

For the compounds examined in this work, attention was paid to collecting chemical shifts, coupling constants and, if possible, the signs of the various couplings. It became apparent that a correlation existed between the orientation of the phosphorus lone pair and the magnitude of couplings to nuclei cis and trans to it and therefore some compounds expected to throw light on the situation were synthesised. It transpired that similar effects had been noticed in some nitrogen compounds[71,72] and also in $PCl_2(NMe_2)$.[73] Other new examples of structurally dependent couplings were also encountered in the course of the work. But this type of relationship only holds true if the molecular geometry is fixed. If at some temperature rotation about the bonds results in other conformations also being populated, then weighted averages of the extreme values of the couplings will be observed, and this phenomemon was also noted.

Chapter 2

Trimethylsilylaminodifluorophosphine

"What is now proved was once only imagin'd"

William Blake, The Marriage of Heaven and Hell.

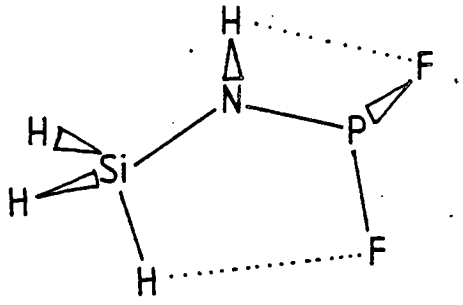
Introduction

The preparation[36] of $PF_2[NH(SiH_3)]$ - equation 2:1 - is quite facile,

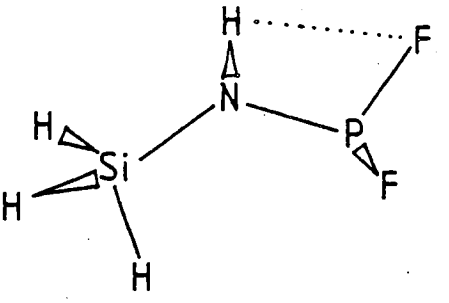
$$3PF_2(NH_2) + 2SiH_3Br \xrightarrow{250\ K} 2PF_2[NH(SiH_3)] + PF_2Br + NH_4Br \quad \ldots\ 2{:}1$$

and the amine is reasonably stable, only decomposing in the liquid phase above 250 K. Examination of the i.r. and Raman spectra, however, revealed that this is a rather unusual secondary amine, for instead of the expected one N-H stretch and one N-H in plane deformation, $PF_2[NH(SiH_3)]$ has two of each type of mode in the gas phase. This was interpreted[36] as due to the presence of two rapidly interchanging conformers - Figure 2:1, a view supported by e.d. studies.

It was decided to investigate whether other similar compounds also showed the same odd i.r. and Raman features. A suitable compound for study would be $PF_2[NH(Si(CH_3)_3)]$. It was expected that this amine would be more stable than $PF_2[NH(SiH_3)]$, as is normally the case with silyl and trimethylsilyl analogs, thus making feasible liquid phase i.r. studies at low temperatures, which proved to be quite helpful. Coincidently, during the course of these studies a co-ordination compound of $PF_2[NH(SiMe_3)]$ was reported, though the amine itself was not isolated[74].



A



B

Figure 2:1 The two conformers found by the gas-phase E.D. study of $PF_2[NH(SiH_3)]$, responsible for the two N-H stretches and bends in the i.r. spectrum.

Results and Discussion

2:1 Preparation

Details of the various preparative methods considered are described in Experimental Sections 2:1 and 2:2. The initial routes investigated were either gas or liquid phase reactions between varying proportions of $PF_2(NH_2)$ and Me_3SiBr (equation 2:2), analogous to the preparation of $PF_2[NH(SiH_3)]$.

$$3PF_2(NH_2) + 2Me_3SiBr \rightarrow 2PF_2[NH(SiMe_3)] + PF_2Br + NH_4Br \quad \ldots 2:2$$

However the lower yields in this case demanded a refinement of the technique, and the addition of NMe_3 as an HBr abstractor to shift the equilibrium to the R.H.S. proved beneficial, equation 2:3.

$$PF_2(NH_2) + Me_3SiBr + NMe_3 \rightarrow PF_2[NH(SiMe_3)] + [NHMe_3]Br \quad \ldots 2:3$$

As with the silyl compound, liquid phase reactions always gave better yields than the corresponding gas phase reaction, while the addition of NMe_3 improved yields by at least an order of magnitude.

The most productive method involved pre-mixing the $PF_2(NH_2)$ with an excess of halide then condensing onto the mixture a slightly lesser excess of NMe_3, and leaving the mixture to react for 10 minutes at ca. 270 K. These base induced reactions were very rapid, even at sub-zero temperatures, and placing an ice-salt bath round the ampoule which was initially at 77 K was the most satisfactory way of achieving the required temperature. No unreacted base was recovered, assumed to be due to the formation of an adduct between NMe_3 and Me_3SiBr.

The compound is volatile and reasonably stable in the gas phase, no signs of decomposition being evident after 10 hours at 310 K, the most testing conditions examined, but after ca. 30 minutes in the liquid phase at room temperature traces of Me_3SiF were detected. Samples became noticably cloudy after 4 days at room temperature and had mainly become a white solid, presumably a P-N polymer, after 7 days. White fumes are produced when in contact with the atmosphere, and if the vacuum line was not scrupulously dry a variety of hydrolysis products was formed, viz: $PF_2(NH_2)$, $O(PF_2)_2$, $O(SiMe_3)_2$ and Me_3SiF, leaving white solids behind, assumed to be mixtures of P-N polymer and NH_4F.

From the n.m.r. spectra it was clear that no $PF_2[N(SiMe_3)_2]$ was formed in any of the preparations. The gas phase molecular weight of $PF_2[NH(SiMe_3)]$ was found to be 156.79 g as opposed to the calculated 157.09 g, which also suggests that no $PF_2[N(SiMe_3)_2]$ was formed. This in unlikely to be due to the expected reduced basicity of the secondary amine, because the presence of NMe_3 should easily overcome this difficulty (see Chapters 3 and 4), but is probably due to steric hinderence of the approach of a second, bulky Me_3SiBr molecule. The tertiary amine has been synthesised, however, by another route by other workers[74].

2:2 $N(SiMe_3)_3$ and PF_2X

The reaction between PF_2X(X=Cl, Br) and $N(SiMe_3)_3$ was investigated with the view to giving easy access to $PF_2(NR^1R^2)$ compounds (R^1 and R^2 = PF_2 or $SiMe_3$). But, as described in Experimental Section 2:3, the amine merely dissolved in the halide at room temperature and the reactants could be recovered

almost totally. Traces of Me_3SiX were observed, probably due to the inevitable traces of HX present from the PF_2X synthesis. No other volatiles were noted even after heating the ampoule.

These results seem a bit perplexing when the facile reaction of PF_2Br with $CH_3CO.N(SiMe_3)_2$ is considered (Chapter 8), but these results are identical to the behaviour of $N(SiH_3)_3$[47] and $PF_2[N(SiH_3)_2]$ (Chapter 4). The bulkiness of the amine may make it so congested as to prevent the formation of the intermediate often suggested[43,46] for such Si-N bond cleavages, while possible $(p\rightarrow d)\pi$ bonding between Si and N may be stabilising the molecule and substantially reducing its basicity, making the intermediate even less favourable.

Excess PF_2Br reacts[75] with $LiN(SiMe_3)_2$ to give only $PF_2[N(SiMe_3)_2]$, and identical reasoning to the above was invoked to account for this. The presence of three possible π-bonding groups in such molecules does tend to produce much stabler and less reactive compounds than molecules with only two such groups.

2:3 Infrared and Raman Spectra

The vibrational spectra of $PF_2[NH(SiMe_3)]$, which are listed in Table 2:1, provide quite good evidence as to the compound's identity. Bands characteristic of the Me_3Si-group are easily recognised. Those at 2960, 2900, 1415 and about 1250 cm^{-1} can be assigned to C-H asymmetric and symmetric stretching, and asymmetric and symmetric bending modes respectively. Part of the band at 850 cm^{-1} may be assigned tentatively to the C-H asymmetric rock, while the C-H symmetric rock is at 780 cm^{-1}. Bands at 696 and 660, 615, 365 and 290 cm^{-1} are usually associated with asymmetric and symmetric SiC_3 stretching modes, and the bend and rocking modes. All these are consistent with other Me_3Si-compounds.[76,77,78]

Table 2:1

Vibrational Spectra of $PF_2[NH(Si(CH_3)_3)]$

Phase	I.R. Gas	I.R. Liquid	I.R. Annealed solid	Raman Solid	Assignment
	3410 W	3375 W	3375 W	3395 VW	νNH
	3350 W	3335 M	3330 M	3355 VW	νNH
	2960 M	2965 M	2970 M	2980 M	$\nu_{as}CH_3$
	2900 W	2910 W	2910 W	2915 W	$\nu_{s}CH_3$
	1415 W	1420 W	1420 W	1416 W	$\delta_{as}CH_3$
	1265 sh, S)	1272 sh, S)	1270 sh, S)	1263 br W	$\delta_{s}CH_3$
	1245 S)	1260 M)	1257 M)		δNH
	1200 S	1215 M	1223 M		δNH
	936 VS	962 S	980 S	992 W) 952 W)	ν_{as}SiNP
	880 sh, VS)	875 sh, S)	871 sh, S)	867 W)	$\rho_{as}CH_3$
	850 VS)	853 S)	855 S)	860 W)	ν_{as}PF
				850 W)	ν_{s}PF
	810 VS	800 S	790 S	796 W)	

continued ...

Phase	I.R. Gas	I.R. Liquid	I.R. Annealed solid	Raman Solid	Assignment
	780 VS	770 S	770 S	765 W	$\rho_s CH_3$
			725 S		
	696 M		696 M	696 VW)	
	660 VW		665 W	662 W)	$\nu_{as} SiC_3$
	615 M		625 M	618 VS)	
				600 VS)	$\nu_s SiC_3$, $\nu_s SiNP$
	505 M	*	565 shm)	500 M	δPF_2
			549 M)		
	365 VW		428 M	417 M	$\rho\ SiC_3$
	315 W		380 W		$\delta\ SiC_3$
	290 VW		326 S	320 W	$\omega\ PF_2$
	250 VW			288 VM	$\delta\ SiC_3$
				234 VW	$\rho\ PF_2$
				193 S	δ SiNP
				123 VW	$\tau\ PF_2$

Ranges studied: I.R.: gas - 4000-200 cm^{-1}, * liquid 4000-750 cm^{-1}, annealed solid 4000-300 cm^{-1}

Raman: 4000-100 cm^{-1}

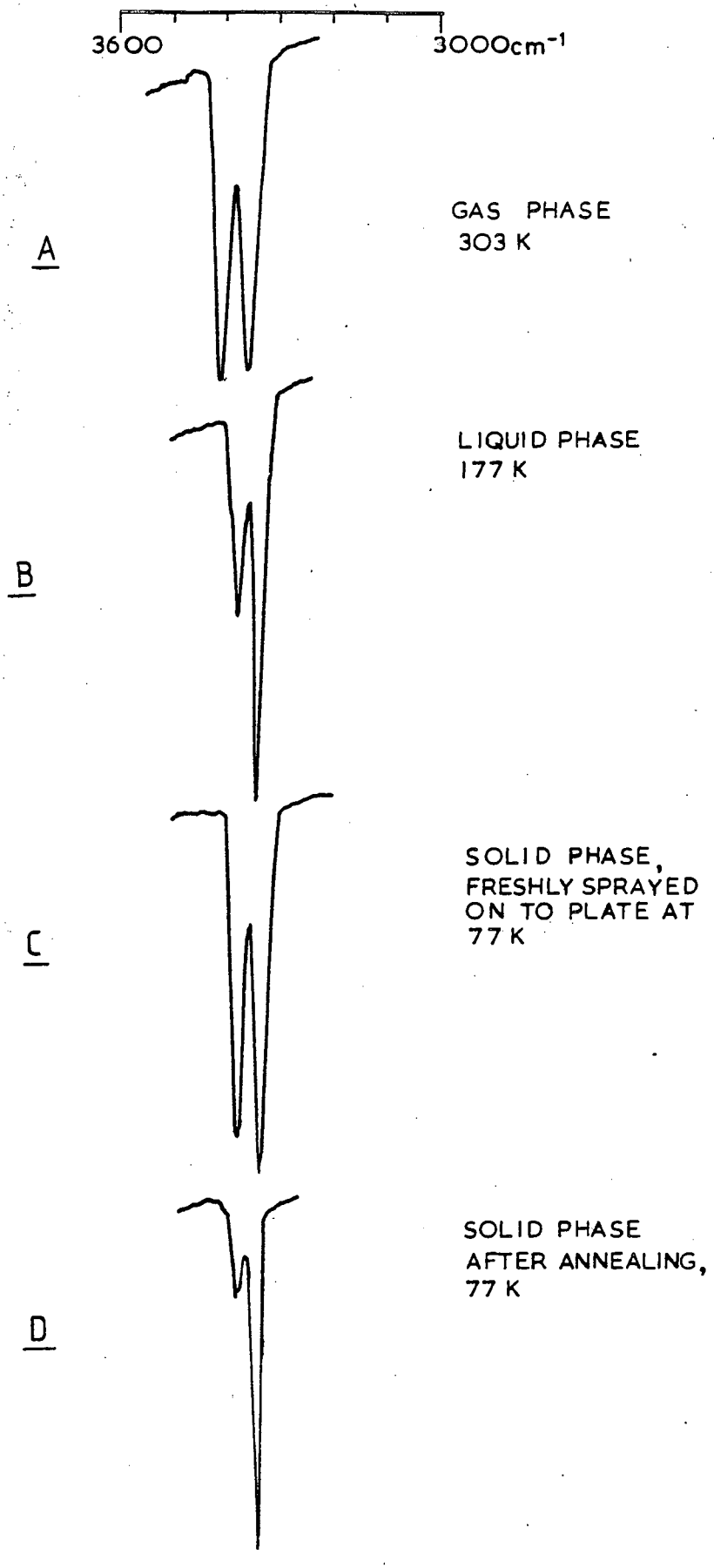

3600
3000cm⁻¹
A
GAS PHASE
303 K
B
LIQUID PHASE
177 K
C
SOLID PHASE,
FRESHLY SPRAYED
ON TO PLATE AT
77 K
D
SOLID PHASE
AFTER ANNEALING,
77 K
ν N-H OF PF2[NH(SiMe3)]

Figure 2:2

For the PF_2 group, the symmetric P-F stretch is easily recognised at 810 cm^{-1} and the asymmetric stretch is part of the broad envelope at ca. 850 cm^{-1} probably the maximum at 880 cm^{-1}, while typical values are assigned to P-F bend, rock and wag modes. Absorptions due to the SiNP group can be assigned with some confidence to the band at 936 cm^{-1} and, with less confidence, to 615 cm^{-1}.

The main point of interest, however, must be the N-H stretches and bends. There are two stretches in the gas phase at 3410 and 3350 cm^{-1}, but only one deformation was noted at 1200 cm^{-1}, with the other presumably masked by the C-H bend at 1250 cm^{-1}. The other N-H deformation mode (presumably 2 bands as well) could not be identified for certain.

Slow interconversion of all the $PF_2[NH(SiH_3)]$ to a single conformation was noted[36] in the solid phase at 77 K, as the bands at 3427 and 3363 cm^{-1} were replaced by one at 3380 cm^{-1}, and the higher frequency band at ~1250 cm^{-1} also disappeared. The gas, liquid, solid, and annealed solid phase spectra of $PF_2[NH(SiMe_3)]$, Figure 2:2, also show the adoption by an increasing proportion of the molecule of one conformation as the temperature is reduced.

In the liquid phase at 177 K the stretches have moved to lower frequency and have sharpened up, which is usually taken as a sign of hydrogen bonding, and the lower frequency band is now three times as intense as the higher one. Samples at 303 K sprayed onto a plate at 77 K (cooled by a reservoir of liquid N_2) showed similar features, but the rapid cooling froze in the ratios of conformers present at some intermediate temperature. Unlike $PF_2[NH(SiH_3)]$, no changes occurred when the sample was left at 77K for 30 minutes, probably due to the bulky Me_3Si group hindering rotation of the PF_2 group in the condensed phase.

The solid sample was annealed by emptying the nitrogen reservoir for short periods and then refilling it. When annealed for 15-20 seconds, the stretches intensity changed to a ratio similar to that in the liquid phase. Carefully repeating the process eventually produced the spectrum of Figure 2:2d, but long annealing periods at higher temperatures gave spectra like Figure 2:2c. In the N-H region of the Raman spectra of liquid and solid samples there were also two peaks whose relative intensities were similar to their i.r. counterparts, though no attempt was made to anneal these samples.

From studies of the vibrational spectra of solid and gaseous $PF_2[NH(SiH_3)]$ and the ratio of conformers found from the e.d. study it was deduced[36] that the higher frequency NH stretch and bend were associated with conformer B. This implies that in $PF_2[NH(SiMe_3)]$, as in $PF_2[NH(SiH_3)]$, the stabler form is A, as the bands associated with this conformer predominate at low temperatures.

The existence of a second molecule with similar properties to $PF_2[NH(SiH_3)]$ is good supporting evidence as to the origin of the doubling of the N-H modes. It is interesting to note that $PF_2(NHR)$ compounds[25] (R = Me, Et, Bu^n and Bu^t) also show two NH stretches and bends in their published spectra, though this appears to have been overlooked, and the phenomenon is obviously more widespread than was first suggested. A recent e.d. study[79] of $PF_2[NH(CH_3)]$ suggests that here too there may be two conformers present.

Some other secondary amines have two N-H stretches, and intramolecular hydrogen bonding was used to explain[80] the postulated two conformers present in α-substituted carboxylic pyrroles, Figure 2:3. Several $NH[P(OR)_2(Y)]R'$ species (Y = O,S) also have two N-H stretches and two conformers.[81]

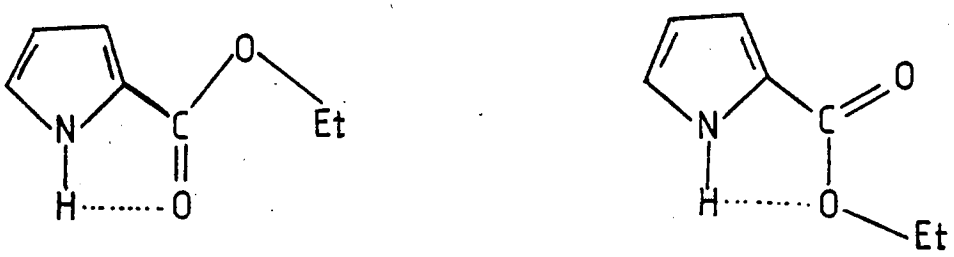


Figure 2:3 The two possible conformations of α-substituted carboxylic pyrroles suggested[80] as giving rise to two N-H stretches and bends in their i.r. spectra.

Table 2:2

Nuclear Magnetic Resonance Data on $PF_2[NH'(Si(CH_3)_3)]$

δH	= 0.19 ppm	$^1J_{PF}$	= 1220 Hz
$\delta H'$	= n.o.	$^1J(C^{13}H)$	= 119 Hz
δF	= -54.25 ppm	$^1J(P^{14}N)$	$\sim$ 40 Hz ($\Rightarrow ^1J(P^{15}N) \sim 56$ Hz)
δP	= +159.6 ppm	$^3J_{FH'}$	= 18 Hz

Solvent: C_6H_6/C_6D_6 n.o. not observed

Temperature: ambient

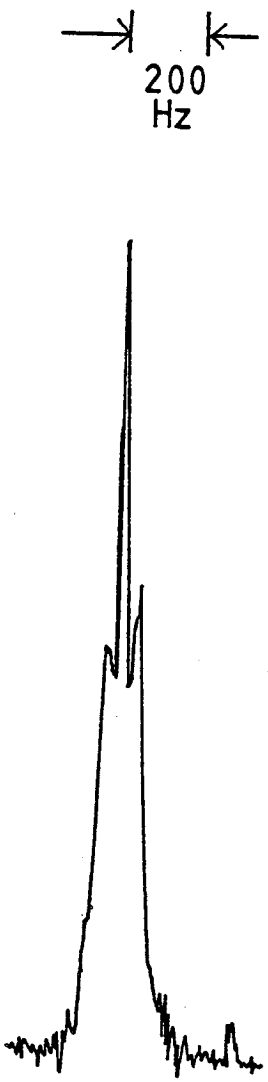


Figure 2:4 Central multiplet of ^{31}P n.m.r. of $PF_2[NH(SiMe_3)]$ showing, for the first time, the resolution of $^{1}J(P^{14}N)$, giving a distorted 1:1:1 triplet.

2:4 N.M.R. Spectra

Chemical Shifts

The presence of a triplet ($^1J_{PF}$) of broad peaks at +159.6 p.p.m. in the ^{31}P n.m.r. spectrum is diagnostic[31] of the presence of a $PF_2N\langle$ compound. The ^{19}F n.m.r. showed only one set of resonances, at δ = -54.25 p.p.m., again characteristic of a $PF_2N\langle$ compound. In the ^1H spectrum the amino proton could not be detected due to ^{14}N broadening, and the Me_3Si-was a not too sharp peak at 0.19 p.p.m. with no resolvable couplings.

Coupling Constants

As can be seen from Table 2:2, few couplings were resolved, mainly due to the broadening effect of the quadropolar ^{14}N nucleus. For the first time ever, ^{31}P - ^{14}N coupling was observed (though since then (1973) a few other $^1J(P^{14}N)$'s have been reported).[82] Such coupling would be expected to result in a 1:1:1 triplet because I = 1 for ^{14}N, but overlap distorts the central line (Figure 2:4). The observed value of $^1J(P^{14}N)$ is rather small as it implies that $^1J(P^{15}N)$ = 56 Hz, whereas $^1J(P^{15}N)$ = 73 Hz in $PF_2(NH_2)$. Resolution of $^1J(P^{14}N)$ implies that the electric field gradient at the ^{14}N nucleus is very small.

Later in this work it will be shown that $^3J_{FH}$, varies, Karplus style, with ∠FPNH', and the value of 18 Hz observed at 223 K agrees with the i.r. spectra's implication that conformer A is adopted at low temperatures, but probably with a greater twist angle for the PF_2 group than in $PF_2[NH(SiH_3)]$.

2:5 Mass Spectrum

With a total of 10 protons to lose, a large number of peaks

Table 2:3

Mass Spectrum $PF_2[NH(SiMe_3)]$

m/e	Intensity	Ion
159	3	$[PF_2[NH_3(SiMe_3)]]^+$, ^{13}C, ^{15}N, ^{29}Si
158	2	$[PF_2[NH_2(SiMe_3)]]^+$, ^{13}C, ^{15}N, ^{29}Si
157	13	$[PF_2[NH(SiMe_3)]]^+$
144	5	$[PF_2[NH_3(SiMe_2)]]^+$, ^{13}C, ^{15}N, ^{29}Si
143	14	$[PF_2[NH_2(SiMe_2)]]^+$, ^{13}C, ^{15}N, ^{29}Si
142	100	$[PF_2[NH(SiMe_2)]]^+$
141	2.5	$[PF_2[N(SiMe_2)]]^+$
138	2	$[PF[NH(SiMe_3)]]^+$
127	3	$[PF_2[NH(SiMe)]]^+$
126	7	$[PF_2[N(SiMe)]]^+$
88	27	$[PF_3]^+$, $[HN(SiMe_3)]^+$
86	4	$[PF_2(NH_3)]^+$, ^{15}N
85	80	$[PF_2(NH_2)]^+$
84	6	$[PF_2NH]^+$
83	6	$[PF_2N]^+$
75	35	$[H_2N(SiHMe_2)]^+$, $[O(SiHMe_2)]^+$
73	28	$[PNSi]^+$, $[SiMe_3]^+$, $[NH(SiMe_2)]^+$
71	20	$?[PF_2H_2]^+$, $[NSi_2]^+$
69	40	$[PF_2]^+$
59	12	$[H_2N(SiMe)]^+$, $[OSiMe]^+$
57	30	$[NSiMe]^+$
46	65	$[PNH]^+$, $[MeSiH_3]^+$

Exact mass:- measured 157.028710

theoretical 157.028817

error <1 ppm

is observed and consequently assignments of all the peaks is impossible, and only the prominent ones are listed in Table 2:3.

The main fragmentation pathways are easily recognised as loss of CH_3 groups, giving the major ion present, at m/e = 142, $[PF_2[NH(SiMe_2)]]^+$, and loss of $SiMe_x$ groups (x = 1,2,3) giving $[PF_2N]^+$ species which pick up some of the many protons available to give $[PF_2(NH_2)]^+$ as the next most important ion. The $SiMe_x$ groups can also pick up protons, and finally, loss of F's and PF_2 groups account for the remaining species observed.

2:6 Photoelectron Spectrum

The He(I) P.E. spectra of $PF_2(NH_2)$, $PF_2[NH(SiH_3)]$, $PF_2[N(CH_3)_2]$ and $PF_2[NH(SiMe_3)]$ are shown in Figure 2:5, while Table 2:4 lists the assignments for these compounds.

Comparing $PF_2[NH(SiMe_3)]$ with the above compounds [84], the first two bands can be assigned to the N and P lone pairs respectively, and the next band is probably the Si-Cσ levels. The rest of the spectrum is a series of broad overlapping bands, from 13.0 to 13.95 eV due to Si-N and C-Hσ levels, 14.7 to 15.6 eV representing N-H and P-Nσ levels, while the highest energy bands are the $F_{2p\pi}$ and P-Fσ levels. All these values are as expected, and none of the bands show vibrational fine structure.

Table 2:4

Photoelectron Spectra of $PF_2[NH(SiMe_3)]$ and Related Species

$PF_2(NH_2)$	$PF_2[NH(SiH_3)]$	$PF_2[N(CH_3)_2]$	$PF_2[NH(SiMe_3)]$	Assignment
10.9	11.0 br	9.6	10.2	$N2p_z$
11.5		10.5	10.55	$P3p_z$
			~11.5	Si-Cσ
	13.0	13.5	13 - 13.95	C-Hσ, Si-Nσ (Si-Hσ, C-Nσ)
15.4	15.2		14.7-15.6	N-Hσ, P-Nσ
16.6	16.8	16.2	16.2	F2pπ
18.0	17.8	17.8	17.2	F2pπ, P-Fσ

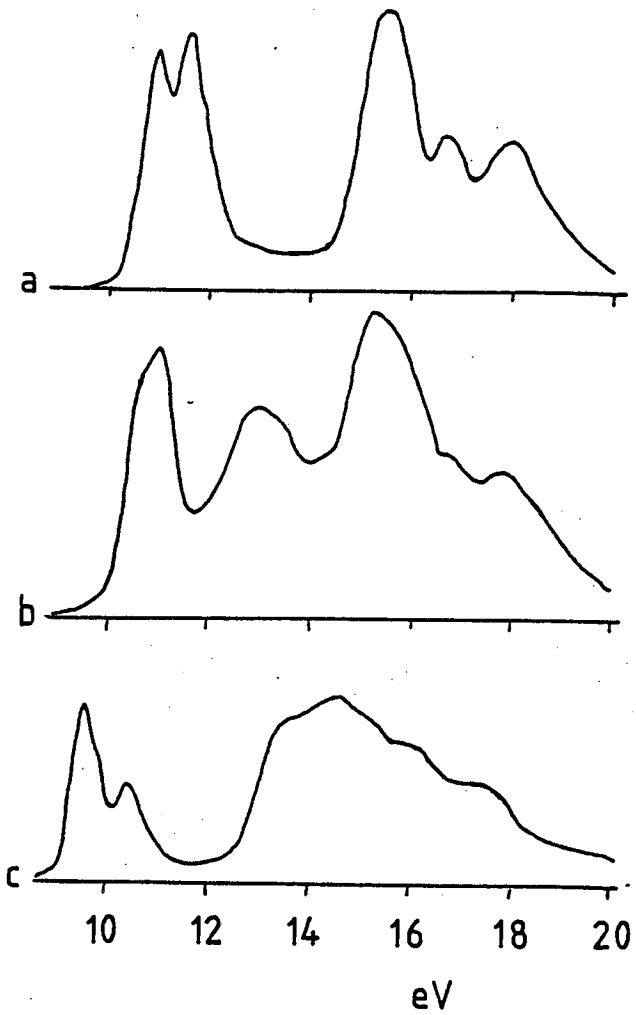


Figure 2:5A Photoelectron spectra of some P-N compounds[83]:
a) $PF_2(NH_2)$, b) $PF_2[NH(SiH_3)]$, c) $PF_2[N(CH_3)_2]$

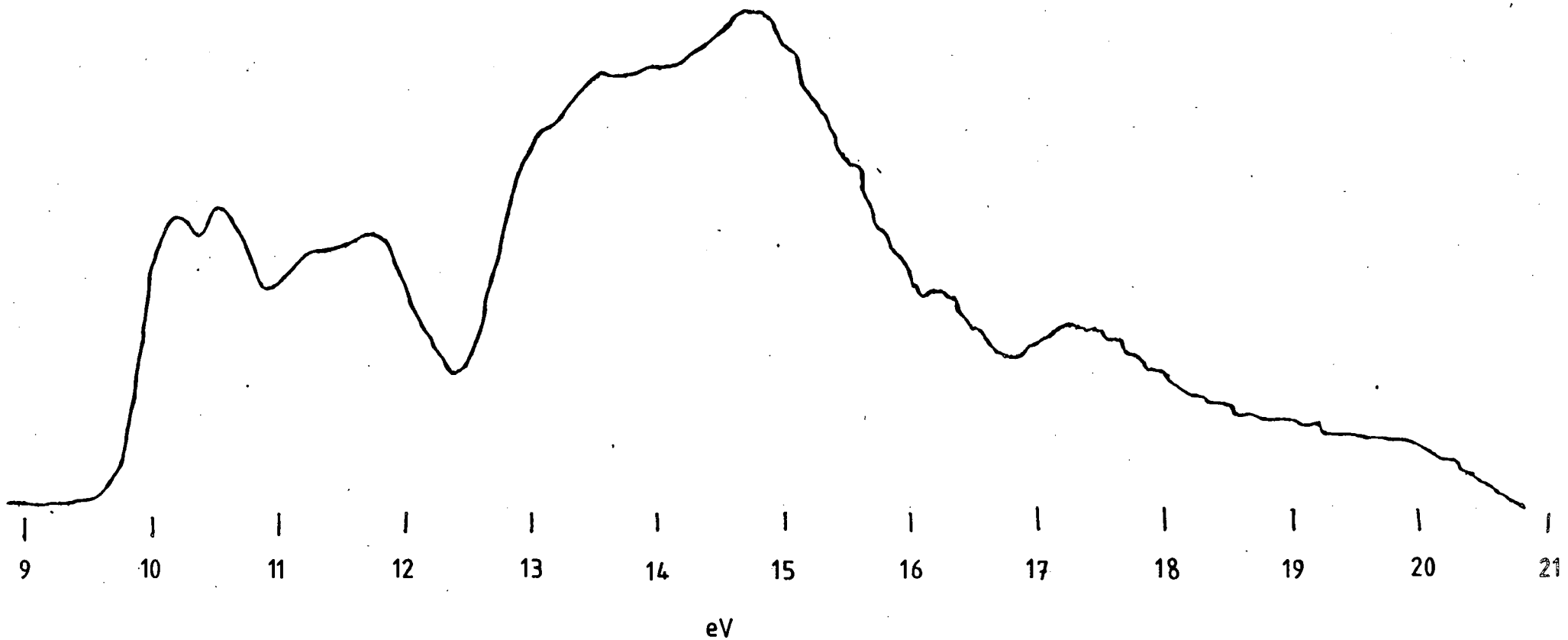


Figure 2:5B Photoelectron spectrum of $PF_2[NH(SiMe_3)]$

Chapter 3

Preparation and Characterisation of Amines Containing Germyl and Difluorophosphino-groups

"It is wise before embarking upon a specific investigation to perform a feasibility study. ... Of course, since those involved are members of the human race, they will probably go ahead and do what they want anyway".

M.I. Davis, "Electron Diffraction in Gases"

Introduction

Having prepared two silylamines both of which have two conformers, other compounds which might have similar properties were sought. The equivalent alkylamines have already been prepared.[25] Moving down the Periodic Table to germanium, it might be expected that $PF_2[NH(GeH_3)]$ would exhibit similar properties to its silyl analogue.

Some trialkylgermyl nitrogen compounds have been synthesised,[85] but when it comes to germyl equivalents of the well known multitude of silylamines (i.e. those with at least one Si-H bond), a slight problem is met - apart from $N(GeH_3)_3$, there are none. Indeed, trigermylamine[45] is extremely unstable and very difficult to handle, decomposing within a few minutes in the gas phase. But the reaction of $PF_2(NH_2)$ and $NH(PF_2)_2$ with germyl halides did produce some interesting results.

Results and Discussion

3:1 Preparation of $PF_2[NH(GeH_3)]$ and $PF_2[N(GeH_3)_2]$

No reaction took place in the gas phase between $PF_2(NH_2)$ and GeH_3X(X=Br,I), although they combined to a small extent (1-2%) in the liquid phase, giving $PF_2[NH(GeH_3)]$, reaction 3:1.

$$3PF_2(NH_2) + 2GeH_3X \rightarrow 2PF_2[NH(GeH_3)] + PF_2X + [NH_4]X \ (X=Br,I) \quad ..3:1$$

These low yields contrast sharply with the preparation[36] of $PF_2[NH(SiH_3)]$, though in both cases the heavier halide gives a higher yield.

When recourse was made to the HX abstractor NMe_3 the liquid phase reactions gave much higher yields, and replacement of both hydrogens by GeH_3 groups also occurred, with the formation of various coloured solids, probably GeH polymers.

$$PF_2(NH_2) + GeH_3X + NMe_3 \rightarrow PF_2[NH(GeH_3)] + [NHMe_3]X \ (X=Br,I) \quad ..3:2$$

$$PF_2[NH(GeH_3)] + GeH_3X + NMe_3 \rightarrow PF_2[N(GeH_3)_2] + [NHMe_3]X \ (X=Br,I) \quad ..3:3$$

The relative proportions of the secondary and tertiary amine naturally varied with the amount of halide used - Experimental Section 3:3. Yields in the ratio 2.5:1 were obtained when a 1.1:1 ratio of GeH_3I to $PF_2(NH_2)$ was used, while a 1:2 yield resulted from a 2.2:1 ratio of halide to amine. It proved much more practical to concentrate on the synthetic route that would give the required amine as the main product, rather than to try to isolate both amines from the same system, although lengthy fractionation procedures were still necessary.

3:2 Preparation of $N(GeH_3)(PF_2)_2$

There was no reaction between $NH(PF_2)_2$ and GeH_3I in either the gas or liquid phase. It has been shown[35] that $NH(PF_2)_2$ is too weakly basic to react with HX, and with no base present the equilibrium for such halide-amine reactions lies to the left. But on addition of NMe_3, Experimental Section 3:4, $N(GeH_3)(PF_2)_2$ formed rapidly - equation 3:4.

$$NH(PF_2)_2 + GeH_3I + NMe_3 \rightarrow N(GeH_3)(PF_2)_2 + [NHMe_3]I \quad ..3:4$$

Addition of the base in two portions results in a higher yield than when adding it all at once by avoiding local excesses of NMe_3 which probably causes side reactions. Repeated fractionation of the products was necessary as $N(GeH_3)(PF_2)_2$ and $NH(PF_2)_2$ are of similar volatility, and the unreacted $NH(PF_2)_2$ was then recycled to yield more $N(GeH_3)(PF_2)_2$. Although from the $NH(PF_2)_2$ taken ~75-80% reaction probably occurred in total, only 28% of the amine was recovered due to decomposition during fractionation. The coloured solids encountered in the preparation of the other germylamines were met here also.

3:3 Preparation of $PF_2[N(GeH_3)(SiH_3)]$

No solids formed until after the addition of NMe_3 to an intimate mixture of $PF_2[NH(SiH_3)]$ and GeH_3I, as described in Experimental Section 3:5,

$$PF_2[NH(SiH_3)] + GeH_3I + NMe_3 \rightarrow PF_2[N(GeH_3)(SiH_3)] + [NHMe_3]I \quad .. 3:5$$

in contrast to the reaction between $PF_2(NH_2)$ and GeH_3I, and this may well be due to the relative basicities of the respective starting materials. However n.m.r. studies showed that the reaction products were complex; besides $PF_2[N(GeH_3)(SiH_3)]$, the following compounds were identified: unreacted starting materials ($PF_2[NH(SiH_3)]$ and GeH_3I), $NH(PF_2)_2$ (a common impurity in these systems), $N(GeH_3)(PF_2)_2$ (presumably formed via equation 3:4), and $PF_2(NH_2)$ (probably from decomposition of $PF_2[NH(SiH_3)]$). No attempt was made to separate a pure sample of $PF_2[N(GeH_3)(SiH_3)]$ from the complex mixture as the compounds would all be of similar volatility, but $PF_2[N(GeH_3)(SiH_3)]$'s identity was established by n.m.r. spectroscopy.

3:4 Stability

Trigermylamine, the only other known germylamine, spontaneously decomposes within a few minutes in the gas phase unless diluted with a large volume of inert gas[45], and cannot be condensed and revapourised without complete decomposition to NH_3 and $(GeH_2)_n$ polymer. In contrast, the amines reported here, although less stable than their silyl analogues, could be handled by more conventional vacuum techniques, though in all cases decomposition was faster in glassware not scrupulously dry and clean.

The least stable of these amines is $PF_2[NH(GeH_3)]$ which decomposes completely in the gas phase within an hour at 290 K and within 10 minutes at 305 K, while in the liquid phase at 209 K, ~33% decomposition occurs within 10 minutes. The compound seemed to be fairly stable in solution at 223 K, decomposition only becoming evident after about 90 minutes. The main decomposition product

is $PF_2(NH_2)$ formed by elimination of GeH_2, and yellow solids, but traces of GeH_4, Ge_2H_6, and GeH_3F were also noted. The solids are probably a mixture of $(GeH_2)_n$ and PN polymers.

$$PF_2[NH(GeH_3)] \begin{cases} \longrightarrow PF_2(NH_2) + \frac{1}{n}(GeH_2)_n & \ldots\ 3{:}6 \\ \longrightarrow GeH_4 + \frac{1}{n}(PF_2N)_n & \ldots\ 3{:}7 \\ \longrightarrow GeH_3F + \frac{1}{n}(PFNH)_n & \ldots\ 3{:}8 \\ \longrightarrow \tfrac{1}{2}Ge_2H_6 + \frac{1}{n}(PF_2NH)_n & \ldots\ 3{:}9 \end{cases}$$

The main route, equation 3:6, resembles the decomposition of $N(GeH_3)_3$ rather than $PF_2[NH(SiH_3)]$ which yields[36] mainly SiH_3F. The faster rates in the more condensed phases are in agreement with the obvious intermolecular interactions necessary for the proposed polymeric products. This instability made it extremely difficult to obtain pure samples, and the spectroscopic data for this compound is therefore incomplete.

While $PF_2[N(GeH_3)_2]$ is somewhat stabler than the monogermyl species, showing no sign of decomposition after four hours in the gas phase at 305 K, solid material was noted after 10 minutes in the liquid phase at 227 K. In solution at 223 K signs of decomposition were noticeable after three hours and n.m.r. spectra indicated that the main route involved elimination of GeH_2 to give $PF_2[NH(GeH_3)]$ which then decomposed as above.

$$PF_2[N(GeH_3)_2] \rightarrow \frac{1}{n}(GeH_2)_n + PF_2[NH(GeH_3)] \quad \ldots\ 3{:}10$$

$PF_2[NH(GeH_3)] \longrightarrow$ as in 3:6 to 3:9

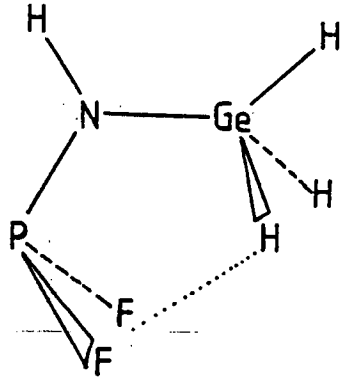
The extra stability of the digermyl species may be associated with the absence of an N-H bond [cf. $N(GeH_3)_3$[45] and the non existance of $NH(GeH_3)_2$] or it may reflect the reduced basicity of the digermyl amine.

Although the stability of $PF_2[N(GeH_3)(SiH_3)]$ could not be studied as pure samples were not isolated, it seemed to be about as stable as the digermyl compound.

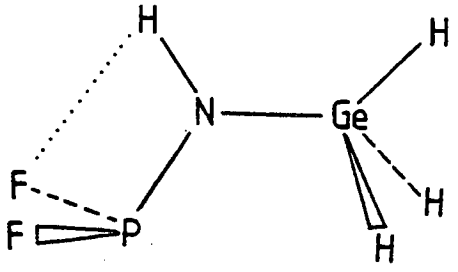
The most stable of the four amines was $N(GeH_3)(PF_2)_2$ which remained almost unchanged as a gas at 305 K for 10 hours. Only on prolonged standing as a liquid at 209 K did solid deposits form, while solutions seemed stable at 223 K for at least five hours. Again the main decomposition route was via elimination of GeH_2, equation 3:11.

$$N(GeH_3)(PF_2)_2 \rightarrow NH(PF_2)_2 + \frac{1}{n}(GeH_2)_n \qquad \ldots 3:11$$

The decomposition of $N(GeH_3)_3$ was found to be base catalysed and the rate increased as the more basic NH_3 was formed. The relative stabilities of the above amines may also be base catalysed and therefore autocatalytic, with the rates of decomposition being dependent on the amine basicity. In turn the basicity is a function of the electron withdrawing character of the substituents, whether by inductive means or by $(p\rightarrow d)\pi$ bonding, germanium having been suggested to participate in $(p\rightarrow d)\pi$ bonding though to a lesser extent than silicon or phosphorus. Decomposition was definitely faster in the presence of more basic impurities such as $PF_2(NH_2)$ or NMe_3 and the slow rate of decomposition of $N(GeH_3)(PF_2)_2$ may be due to the weak basicity of the product $NH(PF_2)$, as well as its own suggested low basicity.



A



B

Figure 3:1 The two possible conformations of $PF_2[NH(GeH_3)]$, suggested by i.r. and n.m.r. data (see also Figure 2:1).

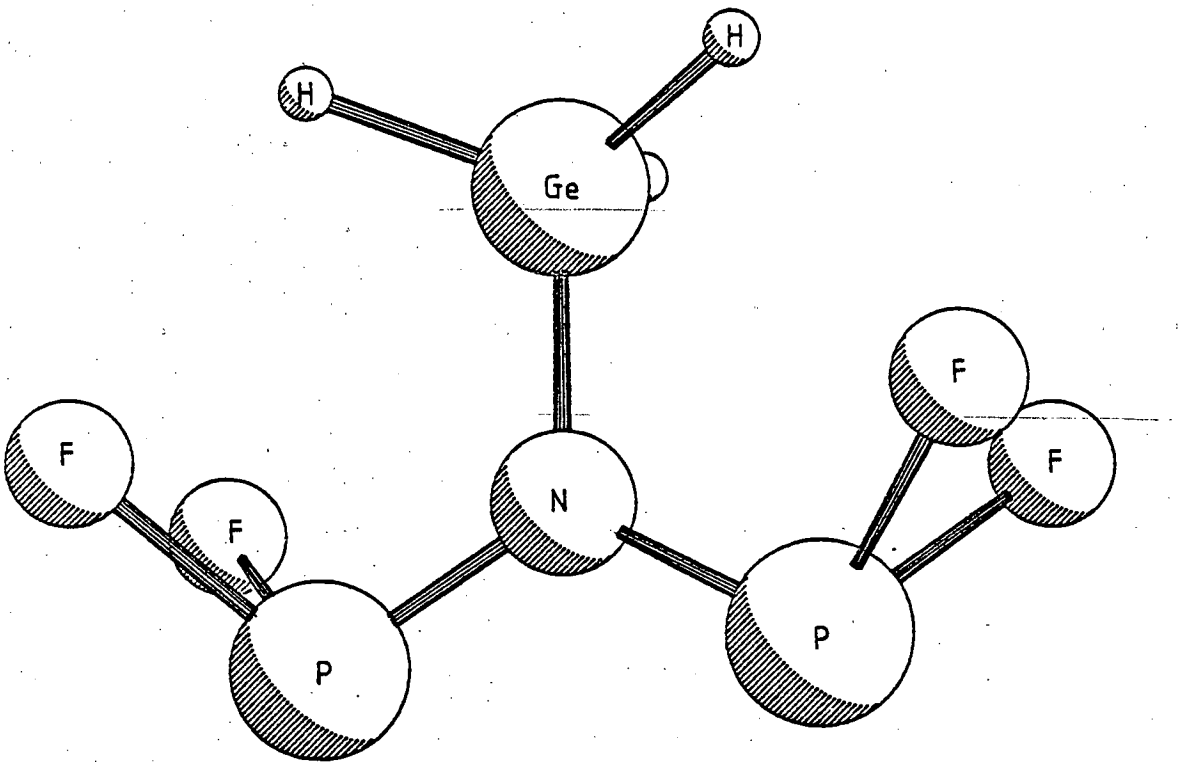


Figure 3:2 Proposed structure of $N(GeH_3)(PF_2)_2$.

However the relative stabilities may also be influenced by intramolecular F--H interactions. The n.m.r. spectra of $PF_2[NH(GeH_3)]$ imply that, at 223 K, there is predominantly one conformation present i.e. the stablest, with F--H(Ge) interactions being an important feature, Figure 3:1. In the most probable conformation of $N(GeH_3)(PF_2)_2$, shown in Figure 3:2 and also strongly supported by the n.m.r. data, there would be four short F--H interactions stabilizing one GeH_3 group, which correctly predicts its increased stability over $PF_2[N(GeH_3)_2]$ which only has two such interactions to stabilize two GeH_3 groups. Coincidently the conformation of Figure 3:2 has since been reported[86] for $N(CH_3)(PF_2)_2$ from gas phase e.d. studies, and a similar structure was found[87] for solid phase $NH(PF_2)_2$.

3:5 Vibrational Spectra

Details of the i.r. spectra of the three amines isolated are presented in Table 3:1, with the Raman spectrum of $N(GeH_3)(PF_2)_2$. Due to the low symmetry of these compounds and the uncertainty of the exact molecular geometry, only a very general, tentative, assignment of the modes in terms of group frequencies can be made, based on typical vibrational frequencies of GeH_3[45,88,89] and PF_2[24,32,35,36] compounds.

The PF_2 stretches, bends, rocks, wags and torsions are easily recognised at the characteristic positions of about 860-840, 450, 360, 290 and 140 cm^{-1} respectively, while the GeH_3 stretches and bends occur at ~2150 and 850 cm^{-1}. The skeletal modes are a bit uncertain, as there are no similar compounds for comparison, and there may be coupling between these vibrations and those of the PF_2 groups. A band at about 1050-950 cm^{-1} is common to many P-N alkyl compounds[24,34,35,90,91] and is often assigned to the C-N stretch. But as this band is present in these germyl derivatives

Table 3:1

Vibrational Spectra (cm^{-1})

$PF_2[NH(GeH_3)]$	$PF_2[N(GeH_3)_2]$	$N(GeH_3)(PF_2)_2$		Assignment
i.r. (gas)	i.r. (gas)	i.r. (gas)	Raman (solid)	
3444 m 3380 w				νNH
2111 s 2096 sh	2120 s 2107 s	2138 s	2162 m 2139 vs	νGeH_3
1225 s 1190 m				δNH
	1005 s	961 s	955 m	νPN, ν_{as}PNP
842 s	862 s	868 s 827 sh	860 s 840 m	νPF_2,
811 vs	820 vs	812 s	792 w	δGeH_3
	774 s			$\nu_s Ge_2N$?
			770 m	$\nu_s P_2N$?
	664 sh			
642 m	655 m	641 m 610 m	648 m,br 630 m,br	ρGeH_3
530 w		572 w	584 m,br 571 m,br	νGeN?
435 w	450 m	465 ms	422 s	δPF_2
	393 w			$\nu_a Ge_2N$?
	308 vw	362 ms 313 w	391 s	ωPF_2
	270 w	296 w	280 w	ρPF_2
			262 m 231 vs 153 w 124 w	$\delta GeNP_2$ and τPF_2

s = strong, m = medium, w = weak, v = very, sh = shoulder,

br = broad.

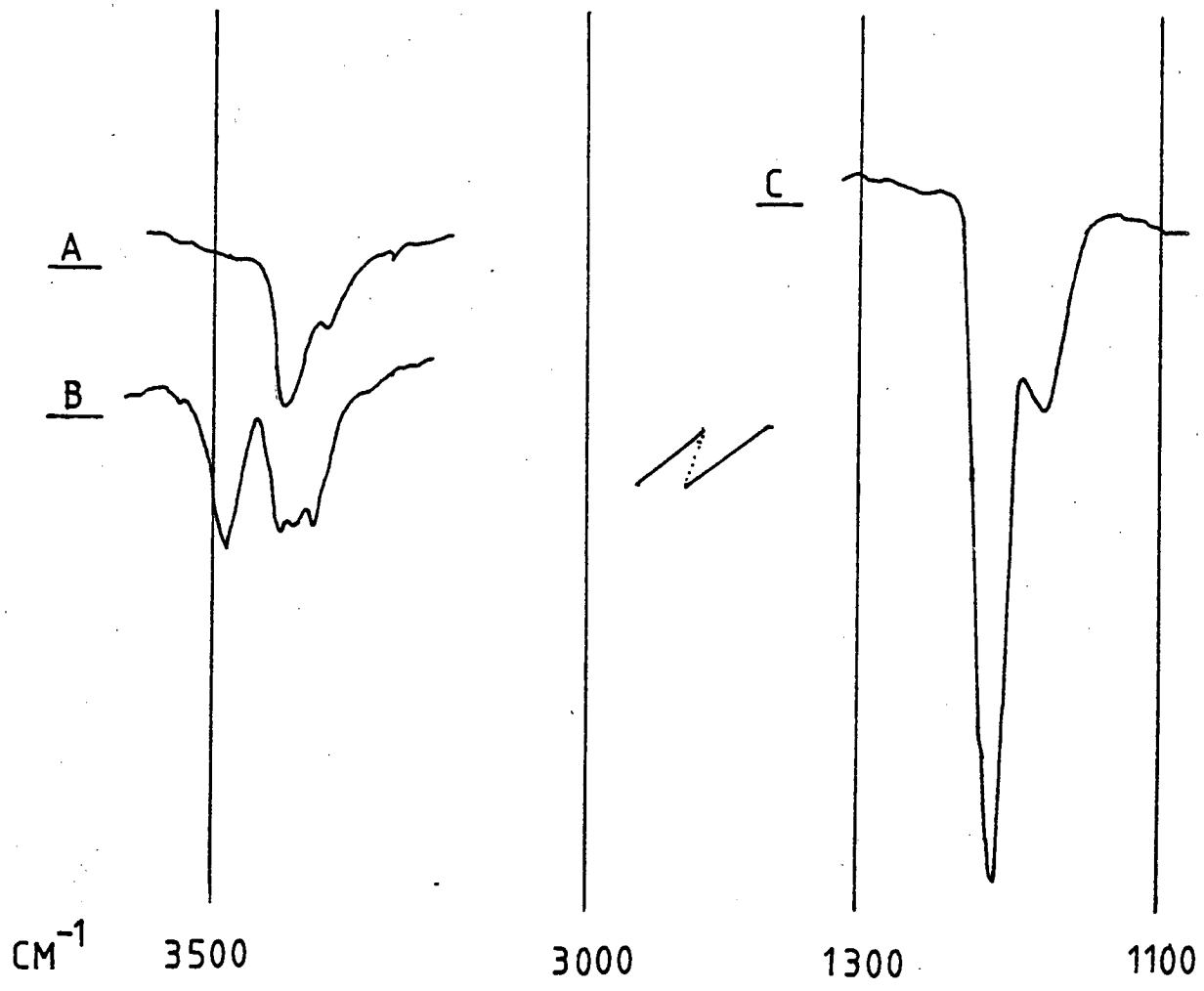


Figure 3:3 Infra red spectrum of gaseous $PF_2[NH(GeH_3)]$, showing two N-H stretches and bends: a) N-H stretch, b) recorded 6 minutes after a), showing rapid decomposition to $PF_2(NH_2)$, c) N-H bend, recorded ∿ 3 minutes after a).

(and their silyl equivalents) an alternative assignment as a P-N stretch is proposed, perhaps coupled with a P-F stretch as suggested[32] for $PF_2(NH_2)$. The remaining low frequency bands are assigned to skeletal modes involving the Ge atom, and these are at lower frequency than in their silyl equivalents (Chapter 4).

The N-H stretching and in-plane deformation bands in the gas phase i.r. spectrum of $PF_2[NH(GeH_3)]$ are the most important features of the spectra. There are two bands in each region, and the higher frequency one of each pair is much more intense than the lower frequency one - Figure 3:3. In the case of the silyl analogue[36], the members of each pair are of almost equal intensity. (The out of plane NH deformation, presumably two bands also, is possibly obscured by the MH_3 band, as happened also in $PF_2[NH(SiH_3)]$ and $NH(SiH_3)_2$[92]). As discussed in the preceding chapter, the higher frequency band of each pair is associated with conformation of Figure 3:1B, with the fluorine atoms interacting mainly with the amino proton and the intensity of the bands in the germyl compounds spectrum suggest that this is the preferred conformer, at room temperature. This seems to contradict the interpretation of the n.m.r. coupling constants, but it is important to remember that the n.m.r. data was recorded at a temperature $\sim 80^{\circ}$ cooler than the i.r. data, and it has been shown for both $PF_2[NH(SiH_3)]$ and $PF_2[NH(SiMe_3)]$ that at low temperatures the molecule adopts the conformation of Figure 3:1A. The instability of $PF_2[NH(GeH_3)]$ ruled out variable temperature n.m.r. and i.r. studies to check for any changes in the predominant conformer with temperature. But perhaps the intensities of the i.r. bands do not reflect the relative populations of the two conformers - the i.r. of $PF_2[NH(SiH_3)]$ suggested

a 1:1 ratio but the e.d. study found a 5:1 ratio of A:B.[36] Similarly, while the i.r. spectrum of $PF_2[NHMe]$ predicts the predominant conformer as one like that of Figure 3:1B, a very recent e.d. study[79] found almost exclusively a conformer akin to Figure 3:1A (but with a greater twist angle of the PF_2 group) as can in fact be predicted from the n.m.r. data.

3:6 N.m.r. Spectra

Possibly the most powerful tool currently available for the rapid elucidation of molecular structure, n.m.r. spectroscopy was used to great advantage in dealing with these germyl amines, due to its ability to handle low concentrations of unstable compounds and mixtures.

Broadening of peaks and loss of resolution due to ^{14}N's quadrupolar nuclear moment was overcome by recording the spectra of the ^{15}N isotopomers, $^{15}NH_3$ being used to synthesise the precursors. The n.m.r. parameters measured are listed in Table 3:2 (see also Figures 3:4 to 3:7), spectra being recorded at 223 K to forestall decomposition of the amines.

The spin system of $^{15}N(GeH_3)(PF_2)_2$ is an $[A[X]_2]_2LQ_3$ type, and the proton decoupled ^{31}P and ^{19}F spectra clearly showed the typical pattern of the A and X parts of an $[A[X]_2]_2L$ system. Such systems have been studied by Lynden-Bell[93,94], Harris[95,96], and Nixon[97], and Figure 3:8 illustrates the coupling constants which may be derived from the line separations, though not all the couplings could be calculated. Spectra of the compounds with only one PF_2 group were all first order, implying that rotation about the P-N bonds must be rapid on the n.m.r. timescale. Fortuitously equal coupling constants resulted in a great deal of overlap of lines in the ^1H

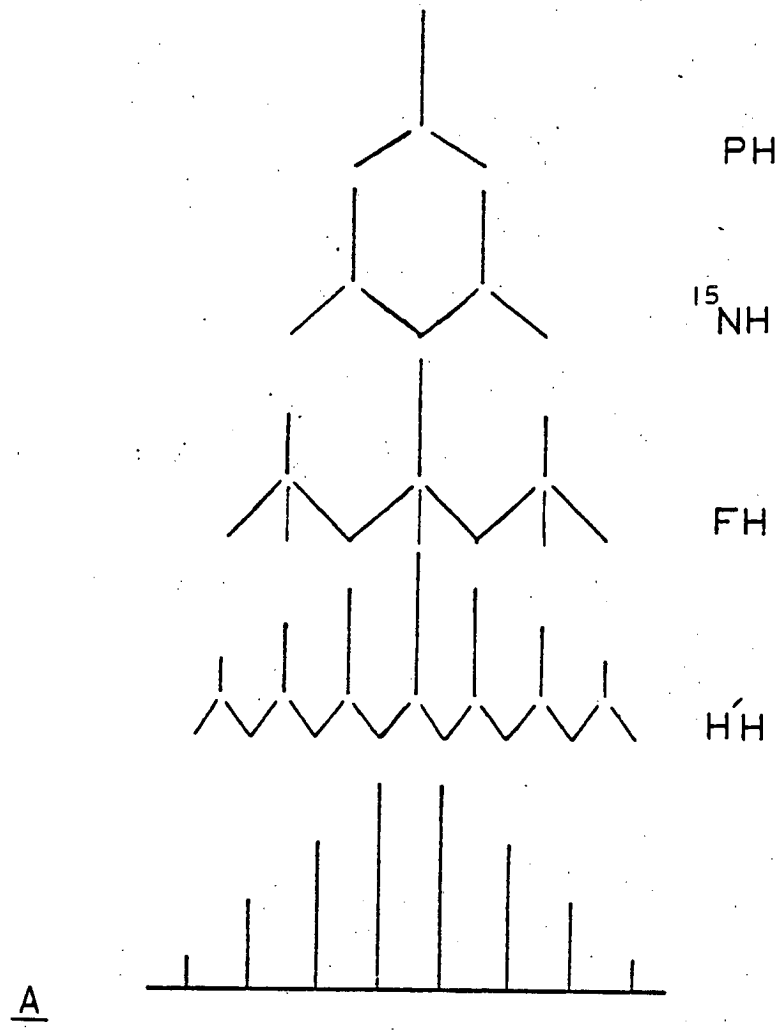
Table 3:2

N.m.r. Parameters

Parameter	$PF_2[^{15}NH'(GeH_3)]$	$PF_2[^{15}N(GeH_3)_2]$	$^{15}N(GeH_3)(PF_2)_2$	$PF_2[N(GeH_3)(SiH_3')]$
δ^1H ppm	4.82	4.92	4.98	4.95
δ^1H' ppm	n.o.			4.35
$\delta^{19}F$ ppm	-55.2	-45.8	-60.6	-48.5
$\delta^{31}P$ ppm	155.1	158.0	149.8	155.5
$\delta^{15}N$ ppm[a]	7.7	-1.4	91.4	n.s.
$^1J_{PF}$ Hz	1200	-1218	-1239	1225
$^1J(P^{15}N)$ Hz	73.5	+82.5	74.0	n.s.
$^2J(^{15}NH)$ Hz	4.6	-4.4	3.5	n.s.
$^2J(F^{15}N)$ Hz	5.6	2.7	4.0	n.s.
$^2J_{PH'}$ Hz	32.7			
$^2J_{PP'}$ Hz			431[b]	
$^3J_{PH}$ Hz	4.6	+9.4	2.0	n.o.
$^3J_{FH'}$ Hz	16.3			
$^3J_{HH'}$ Hz	2.3			
$^3J_{PF'}$ Hz			+15.7	
$^4J_{FH}$ Hz	2.3	+2.9	3.5	n.o.
$^4J_{FF'}$ Hz			n.o.	
$^4J_{FF''}$ Hz			n.o.	

Solvent $CDCl_3$: TMS 1:1 Temperature 223 K

Notes: a. Relative to $[^{15}NMe_4][I]$. b. Varies from 405 Hz (at 303 K) to 442 Hz (at 193 K).



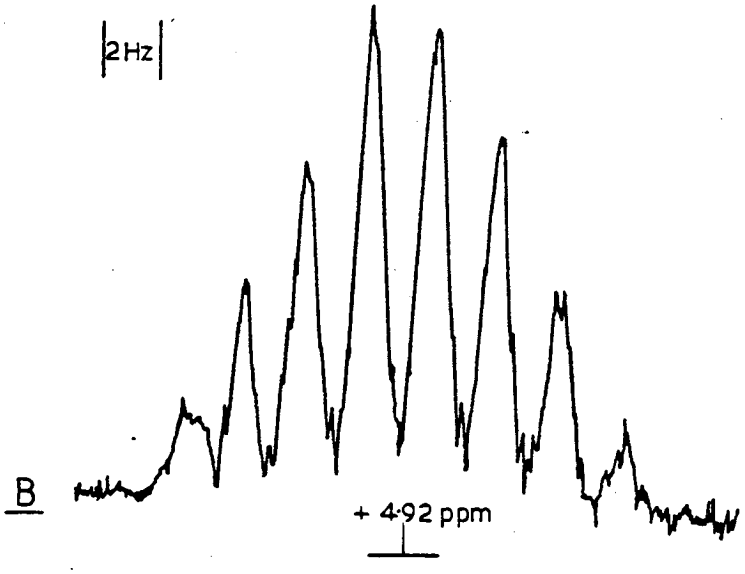


Figure 3:4 ^{1}H n.m.r., GeH_3 region, of $PF_2[^{15}NH(GeH_3)]$.
a) Calculated, b) Observed.

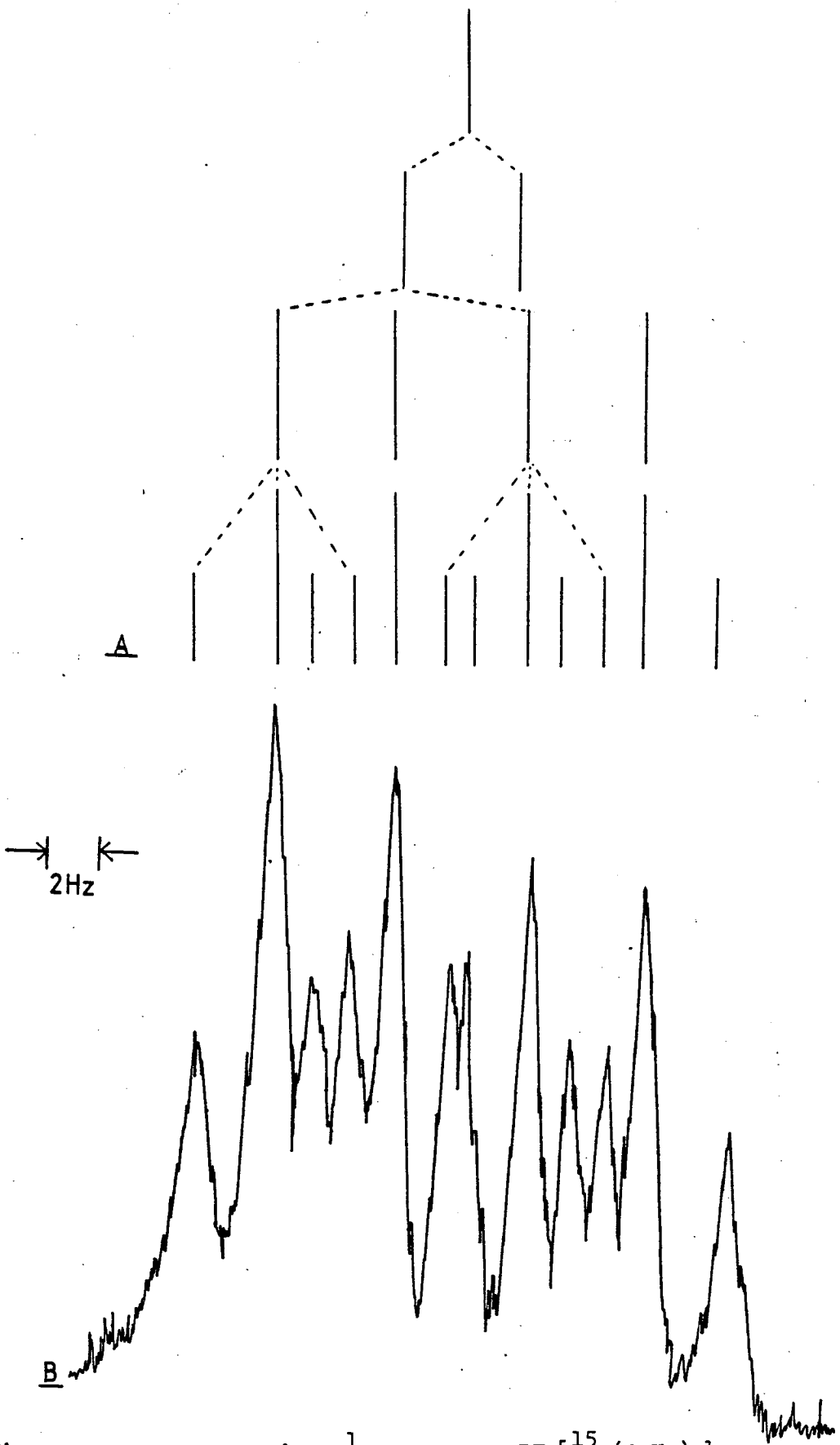


Figure 3:5 A. Theoretical ^{1}H n.m.r. of $PF_2[^{15}N(GeH_3)_2]$.

B. Observed ^{1}H n.m.r.

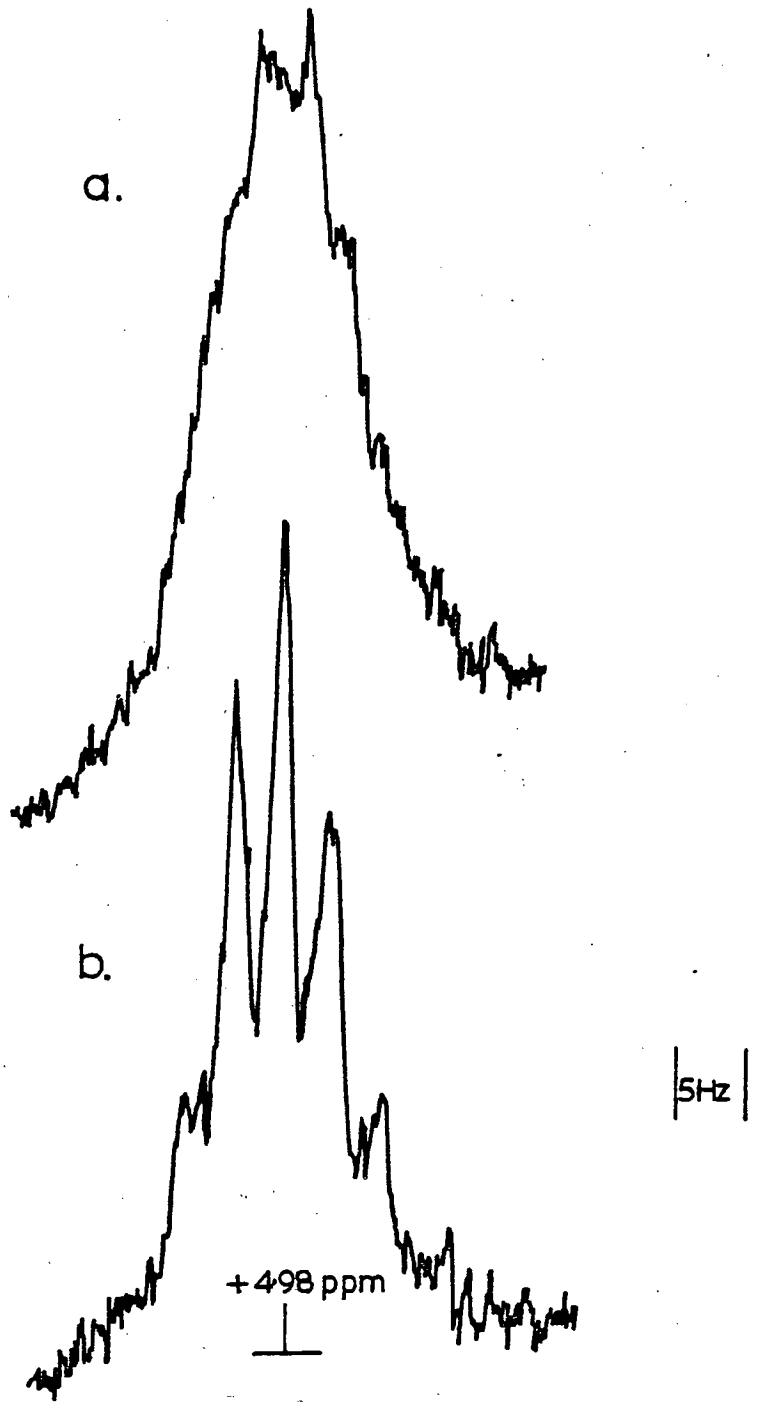


Figure 3:6 A. ^{1}H n.m.r. of $^{15}N(GeH_3)(PF_2)_2$

B. With ^{15}N decoupling.

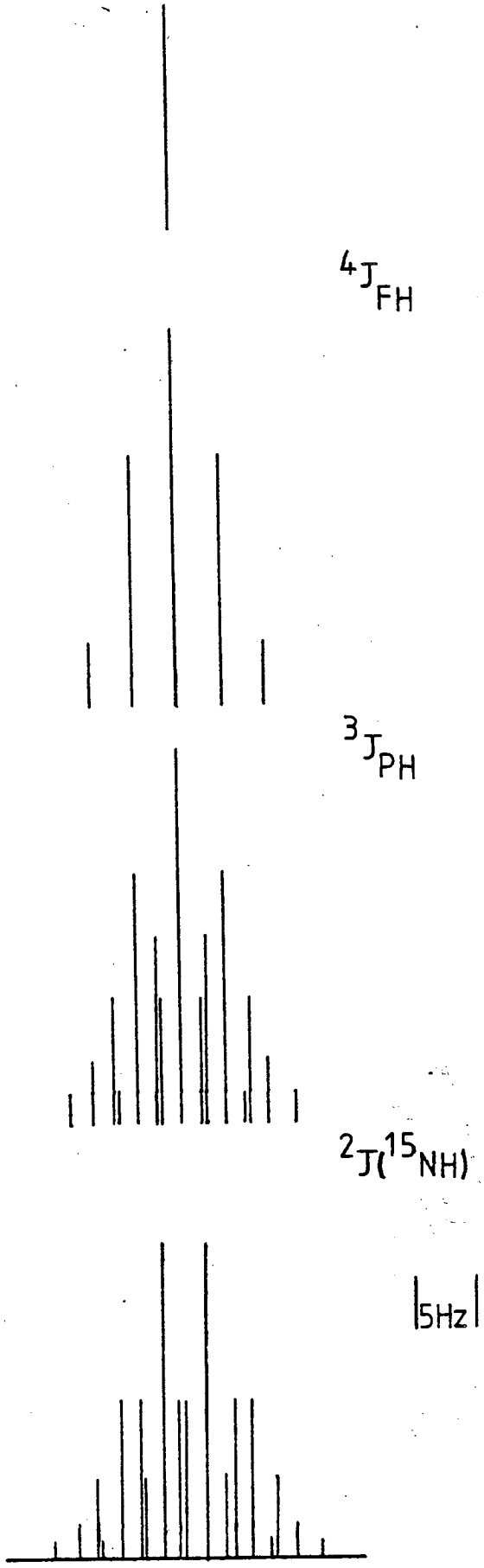


Figure 3:6 C. Calculated ^1H n.m.r. of $^{15}N(GeH_3)(PF_2)_2$

spectrum of $PF_2[^{15}NH(GeH_3)]$ and $^{15}N(GeH_3)(PF_2)_2$ (Figures 3:4 and 3:6).

Chemical Shifts

For all four amines, δP comes within the expected range[31] for F_2PN compounds (+155 to +140 p.p.m.) and the δF's are also typical[31]. Replacement of an H atom by a GeH_3 group results in a high frequency shift of ~5 p.p.m. of the ^{31}P and ^{19}F resonances, compared to the simple difluorophosphinylamines. The GeH resonances are all very similar to that[45] of $N(GeH_3)_3$ (4.91 p.p.m.) and shift to high frequency with increasing electronegativity of the substituents at nitrogen, but the amino proton's resonance in $PF_2[^{15}NH(GeH_3)]$ could not be detected due to the weak, multilined signal being obscured by the presence of $PF_2(^{15}NH_2)$.

The ^{15}N chemical shifts were found by double resonance experiments. Replacement of amino protons in $PF_2(NH_2)$ by GeH_3 groups produced low frequency shifts of $\delta^{15}N$, but for $NH(PF_2)_2$ it caused a high frequency shift.

Coupling Constants

Many of the coupling constants are as expected for this type of compound[31] and help confirm the identity of the various species, the multiplicity of the resonances also being helpful in this respect. Double resonance experiments were useful in confirming the origin of the various couplings, and were especially useful in the case of $PF_2[N(GeH_3)(SiH_3)]$ where the same P and F frequencies, corresponding to resonances in the P and F spectra, affected the SiH and GeH resonances. However some interesting trends were noted which call for further comment.

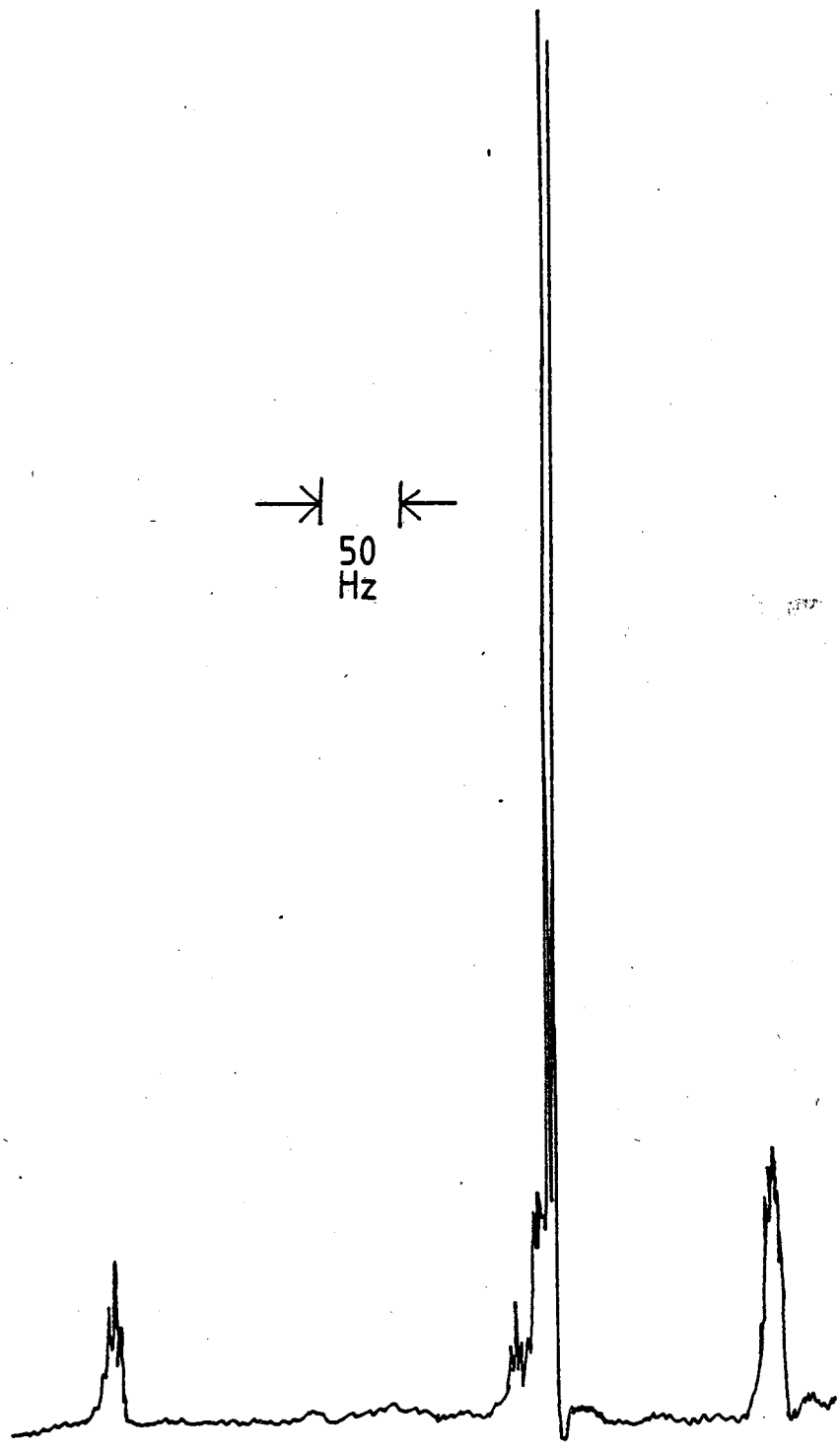


Figure 3:7 ^{19}F n.m.r., high frequency half, ^{1}H decoupled, at 223K, of $^{15}N(GeH_3)(PF_2)_2$, showing the second order $[A(X)_2]_2$ features.

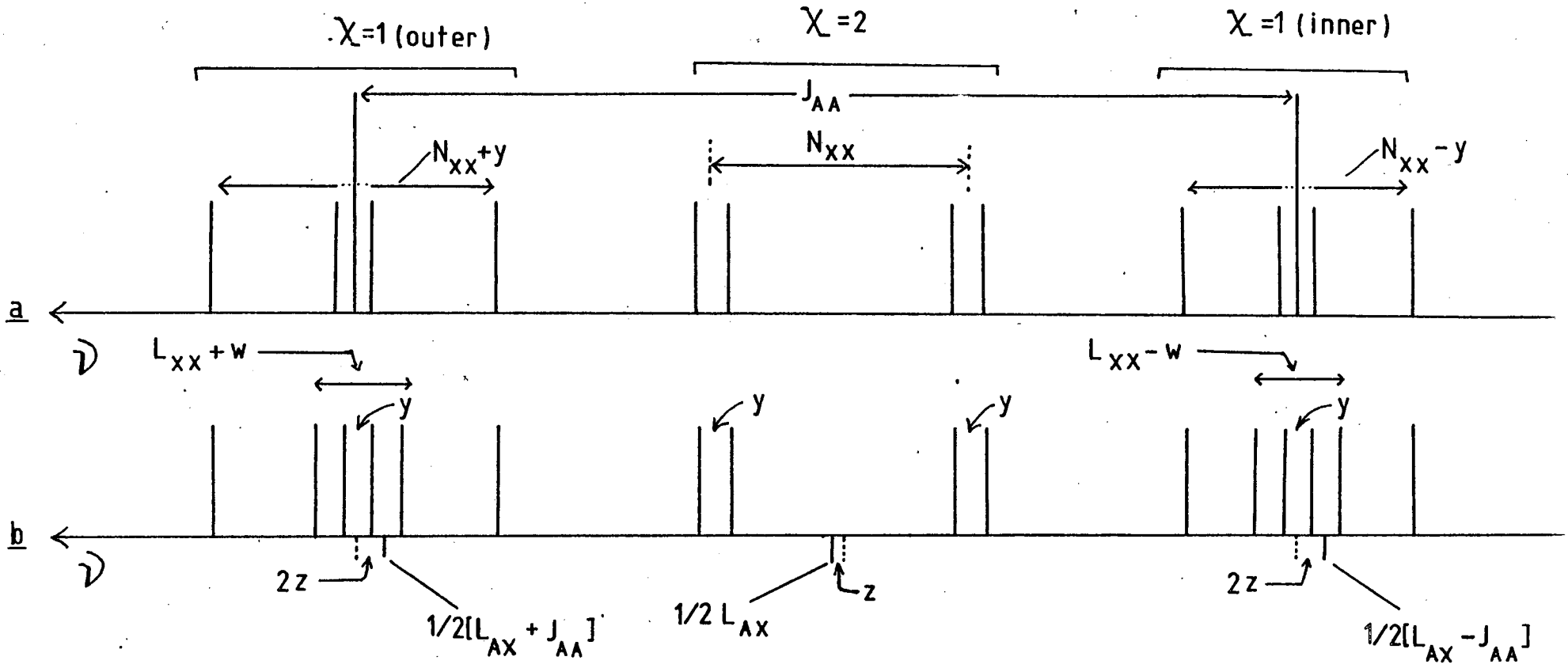


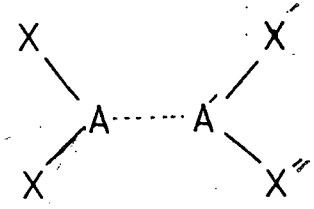
Figure 3:8 a) The $[A(X_2)]_2$ and b) the $[A(X)_2]_2$ second order X n.m.r. spectra, after Harris et al[96].

The intense line at $\frac{1}{2}N_{AX}$ has been omitted.

$N_{AX} = J_{AX} + J_{AX'}$ $N_{XX} = J_{XX'} + J_{XX''}$

$L_{AX} = J_{AX} - J_{AX'}$ $L_{XX} = J_{XX'} - J_{XX''}$

$$w = \frac{J_{AA}.L_{XX}}{L_{AX}} \qquad y = \frac{J_{AA}.N_{XX}}{L_{AX}} \qquad z = \frac{(J_{AA})^2}{8L_{AX}}$$



The value of 32.7 Hz for $^2J_{PH}$ in $PF_2[NH(GeH_3)]$ compares with 18.8 Hz in $PF_2[NH(SiH_3)]$[36] and 18.6 Hz in $PF_2(NH_2)$.[32] It has already been suggested that at low temperatures in molecules such as this the PF_2 group will be orientated to maximise F--H interactions. This could lead to an almost cis relationship between the P lone pair and the amino proton. In a large number of nitrogen[71,72,98,99,100,101,102,103] and phosphorus[73,104,105,106,107,108,109,110] compounds the orientation of a lone pair results in larger couplings to nuclei cis to the lone pair than to those trans - Table 3:3. It does not seem unreasonable to suggest that $^2J_{PH}$ is largest when the P lone pair eclipses the N-H bond, and therefore that $PF_2[NH(GeH_3)]$ exists in solution at low temperatures predominantly in a conformation similar to that of Figure 3:1A. The mixture of conformers due to rotation about the P-N bond in $PF_2[NH(SiH_3)]$ and $PF_2(NH_2)$ results in a weighted average coupling. In[25] $PF_2[NH(CH_3)]$, the large $^2J_{PH}$ = 46 Hz therefore suggests here too the predominant conformation has the P lone pair cis to the amino proton, and this prediction has recently been confirmed[79] by an e.d. study.

If the fluorines in $PF_2[NH(GeH_3)]$ are orientated towards the germyl protons, then the P lone pair is directed away from these protons. Compared to $PF_2[NH(SiH_3)]$ and $PF_2[N(GeH_3)_2]$, $^3J_{PH}$ is small (4.6 Hz) in this compound, as is also the case for $PF_2[NH(CH_3)]$. This coupling also is probably at a maximum when the lone pair is cis to the MH_3 group (M = C, Si, Ge), and is averaged by rotation about the P-N bond in the former two amines, as has already been suggested[73] for $PCl_2[NMe_2]$. At 160 K, inequivalence of $PCl_2[NMe_2]$'s CH_3 groups occurs due to hindered rotation, giving a large and a small $^3J_{PH}$ which average out to the observed coupling at room temperature. This

Table 3:3

The Effect of Lone Pairs on Coupling Constants

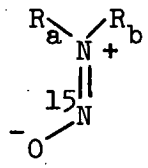
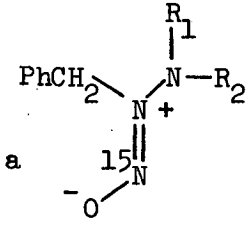
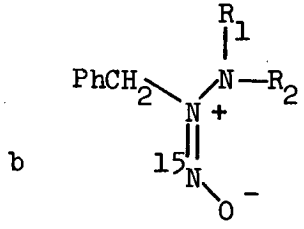
Coupling	Type of Compound	Example	$J_{(NHa)}$ (Hz)	$J_{(NHb)}$ (Hz)	Reference
$^3J(^{15}NNCH)$		$R=PhCH_2$	0	3.1	98
$^3J(^{15}NNCH)$		$R_1=R_2=CH_3$	0	2.2	72
	a 				
	b				

Table 3:3 cont/d..

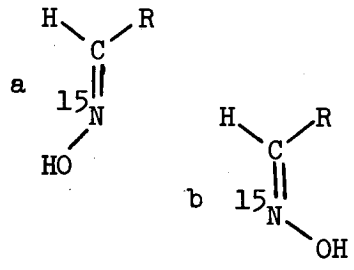
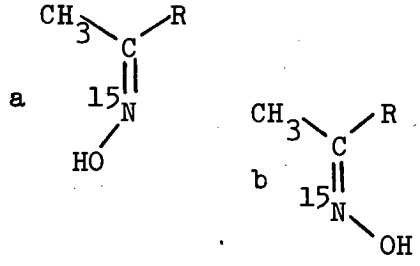
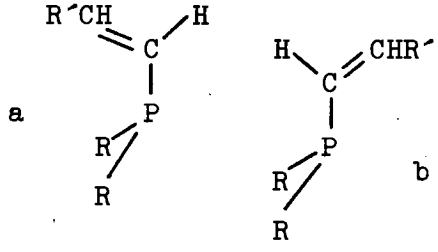
Coupling	Type of Compound	Example	$J_{(NHa)}$ (Hz)	$J_{(NHb)}$ (Hz)	Reference
$^2J(^{15}NCH)$		R=H	+2.6	-13.8	102, 103
$^3J(^{15}NCCH)$		R=H	-2.5	-4.1	103
$^2J_{PCH}$		R=NMe_2 R´=C_6H_6	+25.4	-5.6	104

Table 3:3 cont/d..

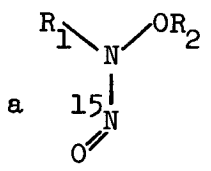
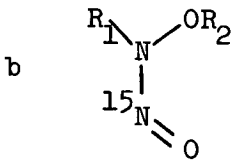
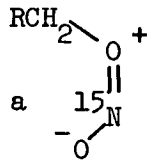
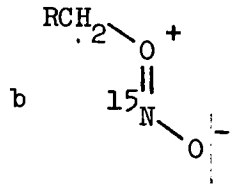
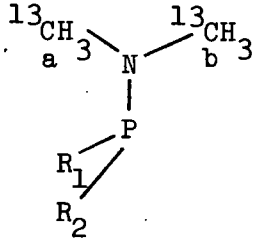
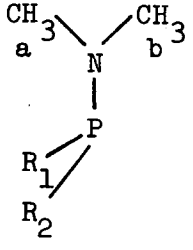
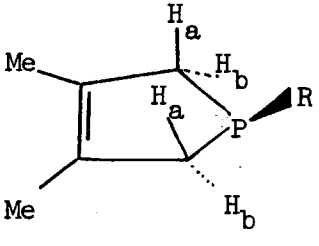
Coupling	Type of Compound	Example	$J_{(NHa)}$ (Hz)	$J_{(NHb)}$	Reference
$^3J(^{15}NNCH)$	a 	$R_1=R_2=CH_3$	0.7	2.0	100
	b 				
$^3J(^{15}NOCH)$	a 	R=Ph	0	2.4	101
	b 				

Table 3:3 cont/d..

Coupling	Type of Compound	Example	$^{J}(PXa)$ (Hz)	$^{J}(PXb)$ (Hz)	Reference
$^{2}J(PN^{13}C)$		R_1=Ph, R_2=Cl	-11.4	+33.9	105
$^{3}J(PNCH)$		$R_1=R_2$=Cl	4.9	19.2	73
$^{2}J(PCH)$		R=Ph	-6	+25	106

hypothesis is supported by the observations that $^3J_{PH}$ for $N(GeH_3)(PF_2)_2$ is even smaller, 2.0 Hz, for this compound probably exists in the conformation of Figure 3:2, with the P lone pairs trans to the N-Ge bond. A similar structure has been found[86] for $N(CH_3)(PF_2)_2$ and a small value of $^3J_{PH}$ is also reported[34]. (In Chapter 4, a similar interpretation is made of the equivalent couplings of the silyl analogues). This interpretation implies that the values normally observed for $^2J_{PH}$ and $^3J_{PH}$ in all compounds like these are in fact a weighted average of a large and a small coupling, perhaps even of different sign, associated with the two extreme orientations of the lone pairs.

If the spectra of $PF_2[N(GeH_3)_2]$ (and $PF_2[N(SiH_3)_2]$, Chapter 4) were recorded at very low temperature, say 150-130 K, then rotation about the P-N bond should become slow enough for the two GeH_3 groups to become inequivalent and two $^3J_{PH}$'s to be resolved. Similarly it might be possible to resolve two $^2J_{PH}$'s for $PF_2(NH_2)$ and $PF_2[NH(SiH_3)]$, if very low temperatures were employed - the latter showed further splittings in its ^1H spectrum at 200 K, too many additional lines to be merely due to two inequivalent fluorines in one conformer [36].

Two other couplings which also seem to be affected by the molecular geometry are $^3J_{FH}$ which appears to obey a Karplus type rule, and $^2J(F^{15}N)$ which is larger when there is an amino proton present in the molecule for the fluorines to interact with. Both these parameters are discussed in more detail in Chapter 5.

The relative signs of the various reduced coupling constants, K, for $PF_2[^{15}N(GeH_3)_2]$ were obtained with the exception of $^2J(F^{15}N)$, while observing the proton spectrum, by a series of double

Table 3:4

Relationship between the signs of the various reduced coupling constants (K) and hence the coupling constants (J) of $PF_2[^{15}N(GeH_3)_2]$

$$^1K(P^{15}N) \not\propto {}^2K(^{15}NH)$$
$$^1K_{PF} \not\propto {}^4K_{FH}$$
$$^1K_{PF} \not\propto {}^3K_{PH}$$
$$^1K(P^{15}N) \not\propto {}^3K_{PH}$$

Assuming $^1K_{PF}$ and $^1J_{PF}$ are negative

then $^4J_{FH}$ is positive
$^3J_{PH}$ is positive
$^1J(P^{15}N)$ is positive
$^2J(^{15}NH)$ is negative.

Table 3:5

Variable Temperature ^{19}F N.m.r. Study of $^{15}N(GeH_3)(PF_2)_2$

Temperature (K)	$^2J_{PP'}$ (Hz)
303	405.0
283	414.8
263	422.5
243	427.4
223	432.7
203	438.3
193	442.1

Other Parameters	303 K	193 K
δF ppm	-60.04	-60.90
$^1J_{PF}$ Hz	1240	1239
$^2J(F^{15}N)$ Hz	3.8	3.9
$^3J_{PF'}$ Hz	16	16

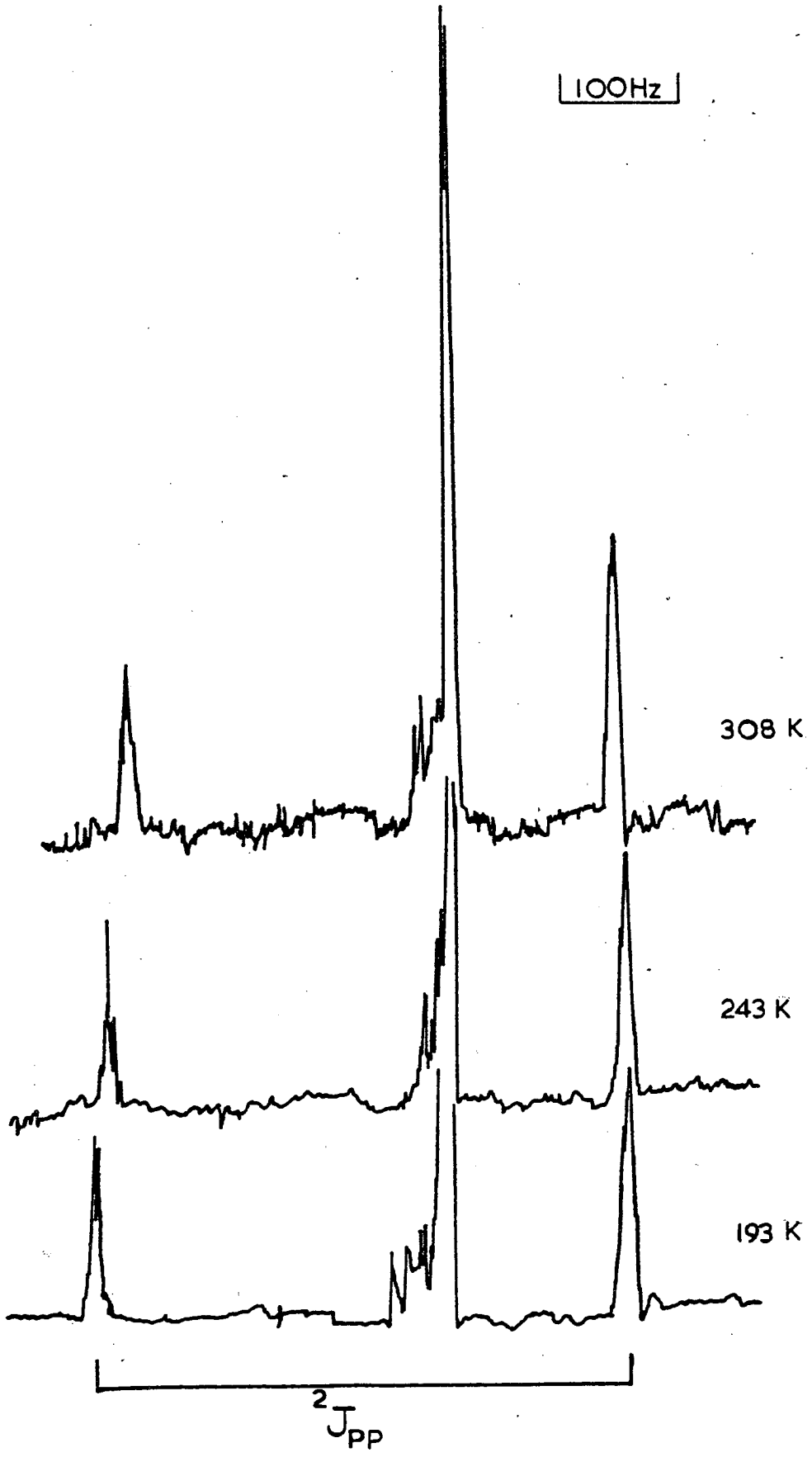


Figure 3:9 Variable temperature ^{19}F n.m.r. spectra of $^{15}N(GeH_3)(PF_2)_2$, high frequency half, ^1H decoupled, showing variation of $^2J_{pp}$.

resonance experiments (Experimental Section 3:6, Table 3:4). Assuming that $^{1}K_{PF}$ is negative [111,112], and bearing in mind the negative gyromagnetic ratio of ^{15}N, the absolute signs of the K's and the J's can readily be determined. The signs agree with those of the equivalent couplings[83] in $PF_2[^{15}NH(SiH_3)]$. The positive value of $^{4}K_{FH}$ may well be due to direct i.e. through-space interactions between the coupled nuclei, for according to the simple alternating rule based on Fermi contact alone, four-bond reduced couplings should be negative. This further strengthens the belief that F--H interactions are important in these molecules.

It is generally held that the Fermi contact mechanism dominates couplings between all nuclei, not just first row elements,[111,113,114,115] and couplings are often interpreted as indicating the s character in a bond[116,117,118,119]. The s character in P-X bonds varies dramatically with the P's oxidation state, being very small for P^{III} compounds where effectively p orbitals are used for bonding. Tetrahedral P^{V} molecules use sp^3 hydrids and have 25% s character, while equatorial bonds (sp^2 hybrids) in five co-ordinate P^{V} have 33% s character and the axial bonds (dp hybrids) have zero s character. This leads to predictable increases in $^{1}K(P^{15}N)$ from negative in P^{III} compounds to positive in equatorial P^{V} species, this having been confirmed in several cases [117,118,119,120]. The negative $^{1}K(P^{15}N)$ in $PF_2[^{15}N(GeH_3)_2]$ can thus be rationalised when at first sight this one bond coupling would be expected to be positive (remembering ^{15}N's negative γ). However the effect upon $^{1}J(P^{15}N)$ of substituting GeH_3 groups for protons follows no obvious trend.

In the variable temperature study of $^{15}N(GeH_3)(PF_2)_2$, Table 3:5, the only parameter to be significantly affected was $^{2}J_{PP}$. Several theories have been proposed to rationalise the wide range of values

observed[69] and the temperature dependence sometimes noted for $^2J_{PXP}$. For example in $Y(PF_2)_2$ (Y = S and Se) and $N(R)(PF_2)_2$ (R = CH_3,GeH_3) large values ~350 Hz are noted which vary significantly with temperature,[121,122] while in $O(PF_2)_2$, $^2J_{PP}$ = 4 Hz and is unaffected by temperature changes[127].

Suggestions that changes in ∠PXP with temperature due to low frequency bending modes were responsible were dismissed[121,124] as $O(PF_2)_2$ and $S(PF_2)_2$ have similar bending frequencies but markedly different behaviour. Changes in the relative populations of various rotomeric forms of the molecules has also been invoked [121,125], but recent e.d. studies of $S(PF_2)_2$ and $Se(PF_2)_2$ at different temperatures found only one conformer present,[126] as did a similar study[86] on $N(CH_3)(PF_2)_2$.

A through-bond mechanism may be responsible for transmitting the coupling[121], but this does not explain why only $^2J_{PP}$ is substantially affected by temperature. Neither can it explain why for cyclic P-N compounds $^2J_{PP}$ is only 10 - 60 Hz[127,128,129] yet there are more through-bond pathways. Similarly in metal complexes[130] of $N(R)(PF_2)_2$ (and PF_2X)[131,132,133] where there are also more coupling pathways, $^2J_{PP}$ is much reduced (or very small) compared to the free ligand.

Keat[125] has suggested that, as with $^2J(P^{13}C)$ and $^3J_{PH}$, $^2J_{PP}$ will also be critically dependant upon the position of one phosphorus relative to the other's lone pair, and variations with temperature are then due to difficult populations of rotomers - but this latter argument has already been ruled out in the cases of $X(PF_2)_2$ (X = S, Se or NMe).

A through-space interaction between the two phosphorus's lone pairs has been postulated by Rankin[35]. On this basis, when

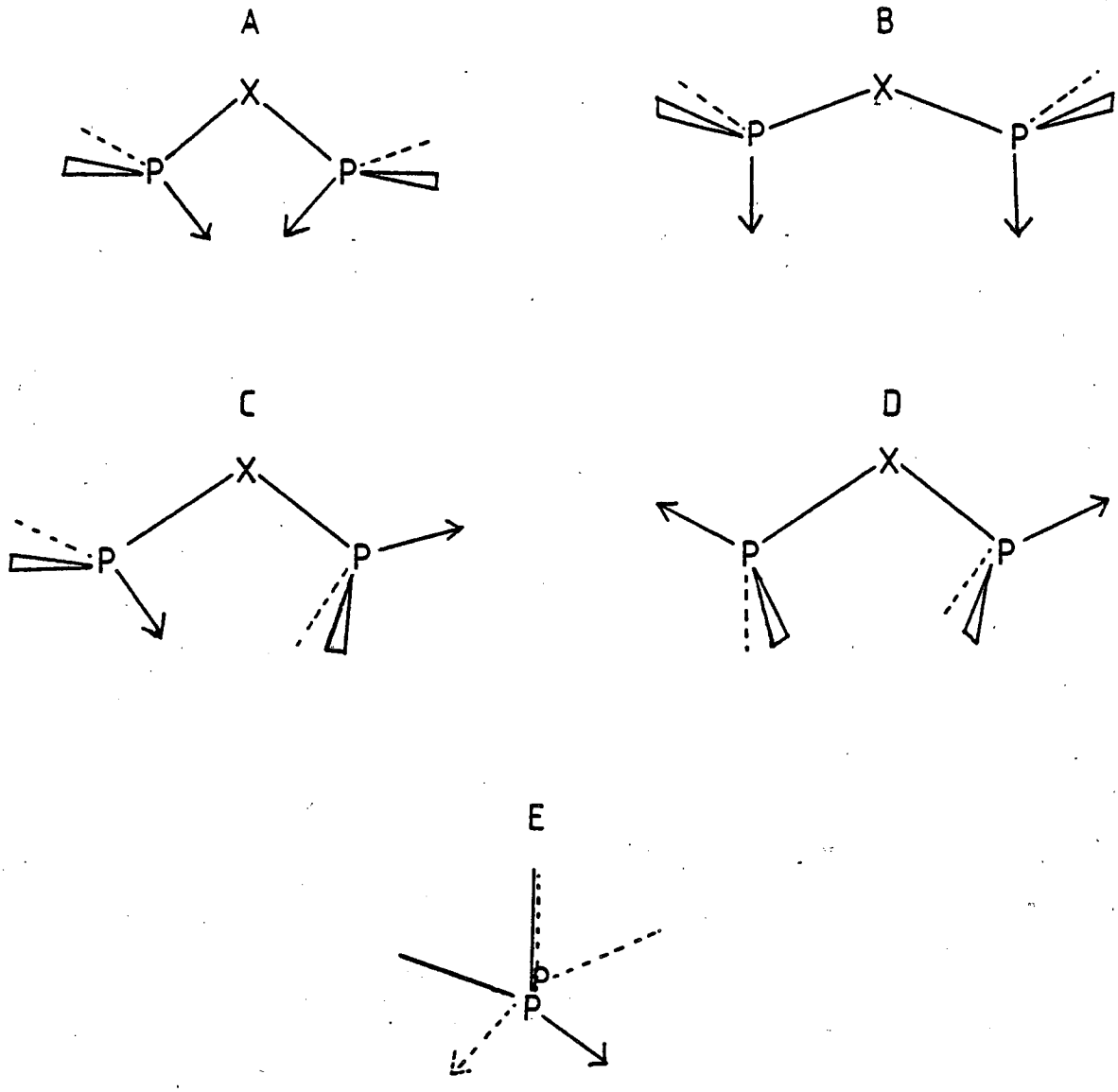
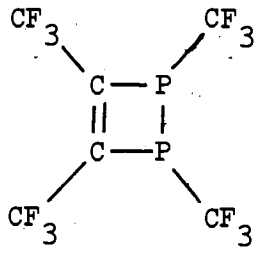


Figure 3:10 The relative orientation of the P lone pairs in various structures.

$\angle$PXP is small, as in[126] $S(PF_2)_2$, the lone pairs come close together in space i.e. the axes of the orbitals converge - Figure 3:10A, and interactions between the electrons cause $^2J_{PP}$ to be large. A wide angle as in[134] $O(PF_2)_2$ keeps the lone pairs further apart, i.e. the axes may be considered to be parallel or to diverge, the interactions are substantially less and $^2J_{PP}$ is small. Variations with temperature result from increases in the amplitude of the torsions of the PF_2 groups which therefore reduce the lone pair - lone pair interactions. When $\angle$PXP is wide, and the lone pairs are not initially interacting, increased torsions cannot further decrease the coupling.

In N compounds, the third substituent on the nitrogen will obviously affect $\angle$PNP. Across the series $N(R)(PF_2)_2$ (R = H, SiH_3, GeH_3) the increase in the size of R should cause $\angle$PNP to subtly decrease, thus increasing the lone pair interactions and conveniently accounting for the increase in $^2J_{PP}$. The increased bulk across the series[125] $Ph_2PNR.PPhCl$ (R = CH_3, Et, Pr^n, Pr^i, Bu^t) however, cannot be accommodated by the angle decreasing indefinitely, but if the PPh_2 and PPhCl groups twisted in opposite directions (Figure 3:10E) this would partly relieve the congestion, decrease the lone pair interactions and account for the decrease in $^2J_{PP}$. The decrease and change of sign between R = Pr^n and Pr^i is most likely due to the molecule becoming so crowded that a different structure, e.g. Figure 3:10C is probably adopted instead.

The small couplings in cyclodiphosph(III)azanes[127] are also easily rationalised for the structure[135,136] of these compounds is such that the axes of the lone pairs do not converge, i.e. there is little interaction. Similarly, the lone pairs axes in



must diverge and this explains why $^{1}J_{PP}$ is only 55 Hz.[137] In metal-phosphine complexes,[133] the lone pairs are involved in bonding and therefore are not free to interact, again explaining the small couplings observed. Replacing a lone pair with, say, oxygen or two fluorines would obviously eliminate such interactions, thus accounting for the small coupling in $P^{III} - X - P^{V}$ and $P^{V} - X - P^{V}$ compounds.[69] The possible structures suggested[35] for $N(PF_2)_3$ are all such as to have no lone pair interactions and $^{2}J_{PP}$ is small here also. Finally $N[CO(CH_3)](PF_2)_2$, as explained in Chapter 8, is likely to have a structure (Figure 8:6a) with no lone pair interactions, and here also $^{2}J_{PP}$ is small.

3:7 Mass Spectra

Because of the instability of these compounds, and their extreme susceptibility to hydrolysis, it was impossible to obtain satisfactory mass spectra, especially for $PF_2[NH(GeH_3)]$, even after purging the equipment with SiH_3Br for an hour. However, $PF_2[N(GeH_3)_2]$ and $N(GeH_3)(PF_2)_2$ were identified by observation of their parent ions, though they were extremely weak, and the isotopic and fragmentation patterns of $X(GeH_3)_2$ and $X(GeH_3)$ were plainly obvious. The $PF_2[N(GeH_3)_2]$ molecule seems to simply fall to bits to every fragment imaginable, including $PF_2[NH(GeH_3)]$ from elimination of GeH_2. The most important breakdown route for $N(GeH_3)(PF_2)_2$ was

also elimination of GeH_2, giving $NH(PF_2)_2$ which then follows its known breakdown pathway [31]. Loss of PF_2 also occurred for these compounds. Interestingly enough, $NH(GeH_3)_2$ and $NH_2(GeH_3)$ were present in all three compounds spectra in quite substantial concentrations, presumably formed by a rearrangement reaction.

3:8 Photoelectron Spectra

The P.E. spectra of $PF_2[N(GeH_3)_2]$ and $N(GeH_3)(PF_2)_2$ were recorded, but the instability of $PF_2[NH(GeH_3)]$ precluded recording its spectrum. Assignments (Table 3:6) were made by comparison with other PF_2N [35,84] and GeH_3 [138,139] compounds.

The lowest energy levels will naturally be the non-bonding N and P lone pairs, but for both molecules these levels overlap somewhat. However the lowest level is always assigned to the nitrogen ^2p_z in PF_2N compounds (cf. $N(GeH_3)_3$, N's ^2p_z = 9.2 eV; PF_3, P's $3p_z$ = 12.2 eV). As in a variety of GeH_3 derivatives,[140,141] the Ge-H σ levels occur at 12.4 eV, which leaves the bands at ∿13.1 eV as the Ge-N σ-level. These bands are at lower I.P. than those of their silyl analogues (Chapter 4). The broad bands at ∿15.3 eV can confidently be allocated to the P-N σ level, in common with other PF_2N compounds, while the highest energy bands are F $2p_\pi$ and P-F σ levels. The variations in band intensity between $PF_2[N(GeH_3)_2]$ and $N(GeH_3)(PF_2)_2$ also confirmed which bands were associated with the PF_2N and $NGeH_3$ parts of the molecule. All of the bands are broad and show no vibrational fine structure.

Table 3:6

Photoelectron Spectra

Ionisation Potential (eV)		
$PF_2[N(GeH_3)_2]$	$N(GeH_3)(PF_2)_2$	Assignment
10.5	10.75	$N2p_z$
11.3	11.0)) 11.6)	$P3p_z$
12.5	12.4	Ge-Hσ
13.2	13.05	Ge-Hσ
15.1	15.45	P-Nσ
16.5	16.0)) 16.8)	F2pπ
17.6	17.4)) 18.3)	P-Fσ

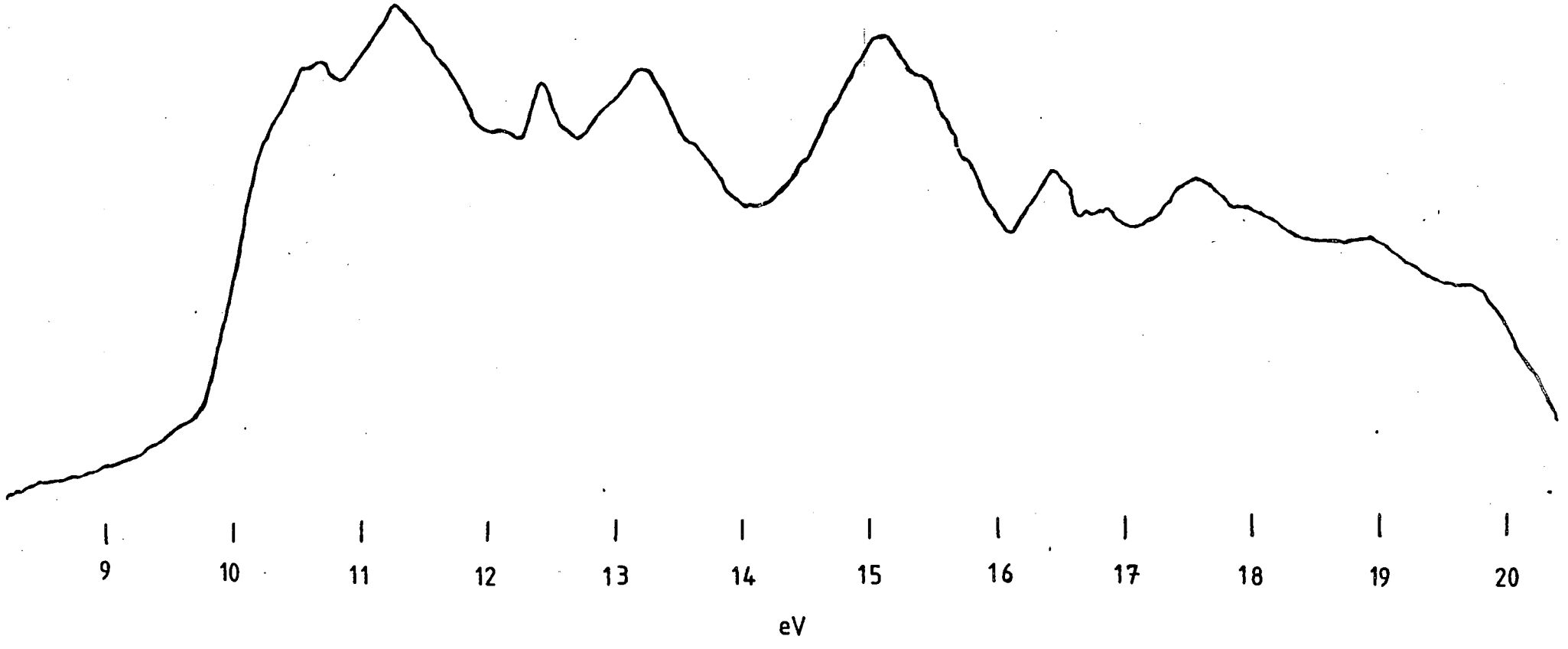


Figure 3:11 A. Photoelectron spectrum of $PF_2[N(GeH_3)_2]$.

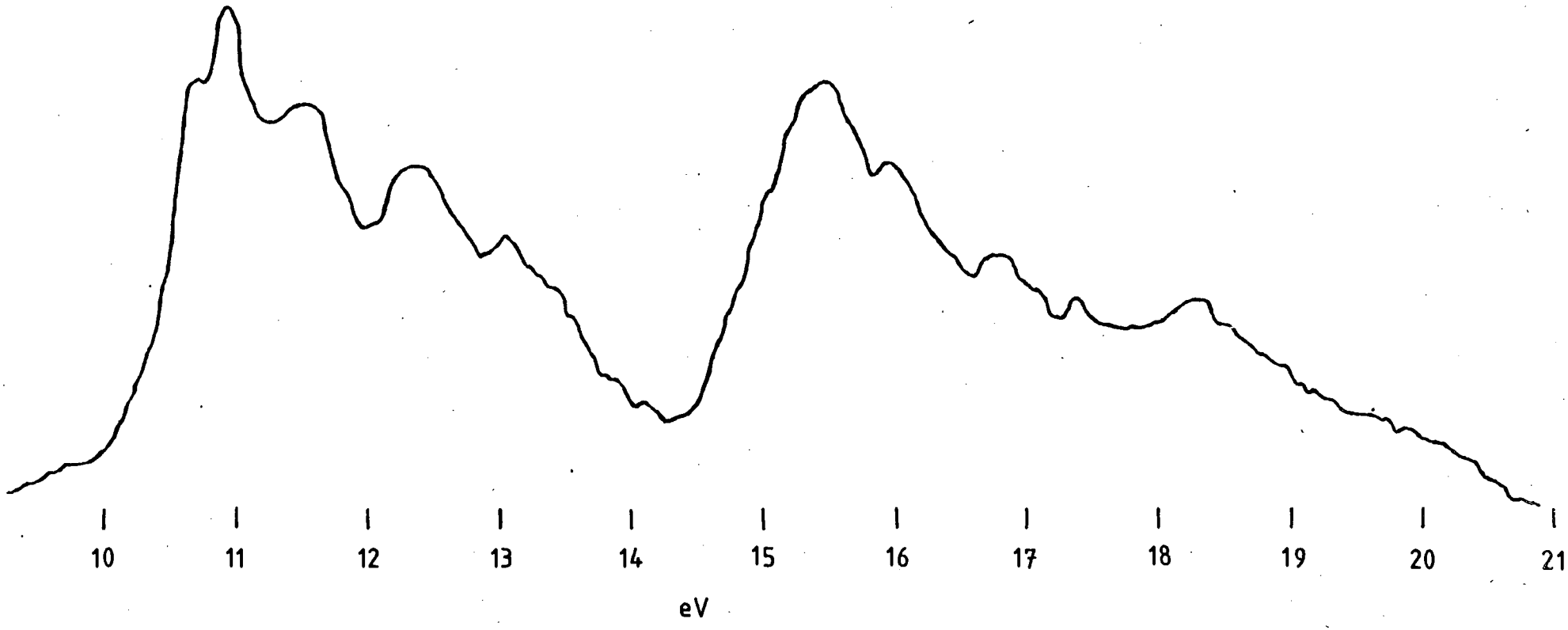


Figure 3:11 B. Photoelectron spectrum of $N(GeH_3)(PF_2)$.

Chapter 4

Preparation and Properties of (Disilylamino) difluorophosphine and Bis(difluorophosphino)silylamine

"Mad, bad, and dangerous to know"

Lady Caroline Lamb.

"Only those who brave its dangers

comprehend its mystery"

H.W. Longfellow

"The Secret of the Sea".

Introduction

When $PF_2[NH(SiH_3)]$ was first prepared[36], no evidence could be found for the existence of $PF_2[N(SiH_3)_2]$ as a by-product. The formation of $PF_2[N(GeH_3)_2]$ and, more significantly, $PF_2[N(GeH_3)(SiH_3)]$ (Chapter 3), and the large number of silicon-nitrogen compounds already reported[43,44], suggested it might be possible to synthesise the tertiary silyl equivalents of the germyl amines of Chapter 3, especially as it has been shown that NMe_3 can overcome the suggested reduced basicity of $PF_2[NH(SiH_3)]$, and silyl halides usually react to replace all the amino protons in a molecule[44].

Results and Discussion

4:1 Preparation of $PF_2[N(SiH_3)_2]$

Not surprisingly, no reaction took place between $PF_2[NH(SiH_3)]$ and SiH_3Br in the liquid phase after 15 minutes at 293 K. Steric hindrance can be ruled out as the more crowded molecules

$PF_2[N(SiMe_3)_2]$[74] and $N(SiMe_3)_3$[142] can be prepared. The suggested reduced basicity of $PF_2[NH(SiH_3)]$ relative to $PF_2(NH_2)$, perhaps due to $(p\rightarrow d)\pi$ bonding, is a more feasible explanation; this might easily be overcome by NMe_3.

The preparation of $PF_2[N(SiH_3)_2]$ according to equation 4:1,

$$PF_2[NH(SiH_3)] + SiH_3Br + NMe_3 \rightarrow PF_2[N(SiH_3)_2] + [NHMe_3]Br \quad ..4:1$$

as described in Experimental Section 4:2, is a rapid, low temperature, liquid phase reaction which presented few difficulties. Pre-reaction adduct formation between NMe_3 and SiH_3Br was partially overcome by mixing the fluorophosphine and the halide before adding the NMe_3, a technique found to be useful with the germylamines. Separation of NMe_3 from the product was unnecessary if excess bromide was present to form the above adduct. It was more convenient to re-react the resultant mixture of $PF_2[NH(SiH_3)]$ and $PF_2[N(SiH_3)_2]$ to force the reaction to completion (cf. $N(GeH_3)(PF_2)_2$ synthesis) than undertake prolonged fractionation, though the mixture was not inseparable. The extent of initial reaction was estimated by i.r. to be ~85%, and the ratio of halide to secondary amine was increased to ~3:1 to increase the likelihood of reaction in the now diluted systems (other ratios tried were less productive). The overall yield obtained after the recycling procedure was 77-80%, based on $PF_2[NH(SiH_3)]$ taken.

It should be pointed out that since the $SiH_3Br.NMe_3$ adduct reacts rather violently with O_2, H_2O, and acids, cleaning out the reaction vessel was quite an interesting experience as it usually involved a minor explosion at some unexpected moment, though never serious enough to shatter the ampoule. This was one very good reason for adhering to small-scale reactions.

4:2 Preparation of $N(PF_2)_2(SiH_3)$

As expected, no reaction occurred between $NH(PF_2)_2$ and SiH_3Br, just as happened with the equivalent germyl reaction, due to the amine's low basicity. Consequently the product cannot be prepared by this direct route.

The subsequent addition of the HBr scavenger NMe_3 to a mixture of $NH(PF_2)_2$ and SiH_3Br results in a very rapid liquid-phase reaction, affording the desired amine in high yield - 87% - according to equation 4:2.

$$NH(PF_2)_2 + SiH_3Br + NMe_3 \rightarrow N(PF_2)_2(SiH_3) + [NHMe_3]Br \quad ...4:2$$

As with $PF_2[N(SiH_3)_2]$, excess halide and a lesser excess of base tends to produce the best results. Large scale preparations are less productive due to inefficient mixing of the reactants, large local excesses of NMe_3 being undesirable. In common with the previous preparation, cleaning the dirty reaction vessel could be an exhilerating experience.

4:3 N.M.R. Spectra

As with the germyl compounds, it was necessary to prepare the ^{15}N isotopomers to resolve many of the coupling constants and to facilitate accurate chemical shift measurements, as well as providing definitive proof of their identity.

At 223 K the spectra of $PF_2[^{15}N(SiH_3)_2]$ are all apparently first order, though it is expected that second order effects would be noticed at very low temperatures due to slowing of rotation about the P-N bond, as was also suggested in the germyl case. The spin system of $^{15}N(PF_2)_2(SiH_3)$ is an $Q_3\ L[A[X]_2]_2$ type and the

Table 4:1

N.m.r. Parameters

Parameter	$PF_2[^{15}NH(SiH_3)]$ [a]	$PF_2[^{15}N(SiH_3)_2]$	$^{15}N(PF_2)_2(SiH_3)$
δ^1H ppm	+4.35	+4.42	+4.39
$\delta^{19}F$ ppm	-56.0 [b]	-51.6	-62.3
$\delta^{31}P$ ppm	+152.6 [b]	155.7	150.0
$\delta^{15}N$ ppm	+14.1	7.1	n.s.
$^1J_{PF}$ (Hz)	-1215.6 [b]	-1237	-1255
$^1J(P^{15}N)$ (Hz)	+72.7 [b]	+77.5	74.6
$^1J(^{29}SiH)$ (Hz)	-224	228	232
$^2J(F^{15}N)$ (Hz)	-4.2	-2.6	3.2
$^2J(^{15}NH)$ (Hz)	-4.1	-3.8	3.5
$^2J(P^{29}Si)$ (Hz)		25	7
$^2J_{PP'}$ (Hz)			367.6
$^3J_{PH}$ (Hz)	+8.0	+9.3	3.5
$^3J(^{29}SiF)$ (Hz)		7.5	11.6
$^3J_{PF}$ (Hz)			+24.9
$^4J_{FH}$ (Hz)	+2.1	+2.9	3.7
$^4J_{FF'}$ (Hz)			3.7
$^4J_{FF''}$ (Hz)			8.0
Temperature	300 K	223 K	238 K
Solvent	CCl_3F-$SiMe_4$	$CDCl_3$-$SiMe_3$ (3:1)	$CDCl_3$-$SiMe_4$ (3:1)

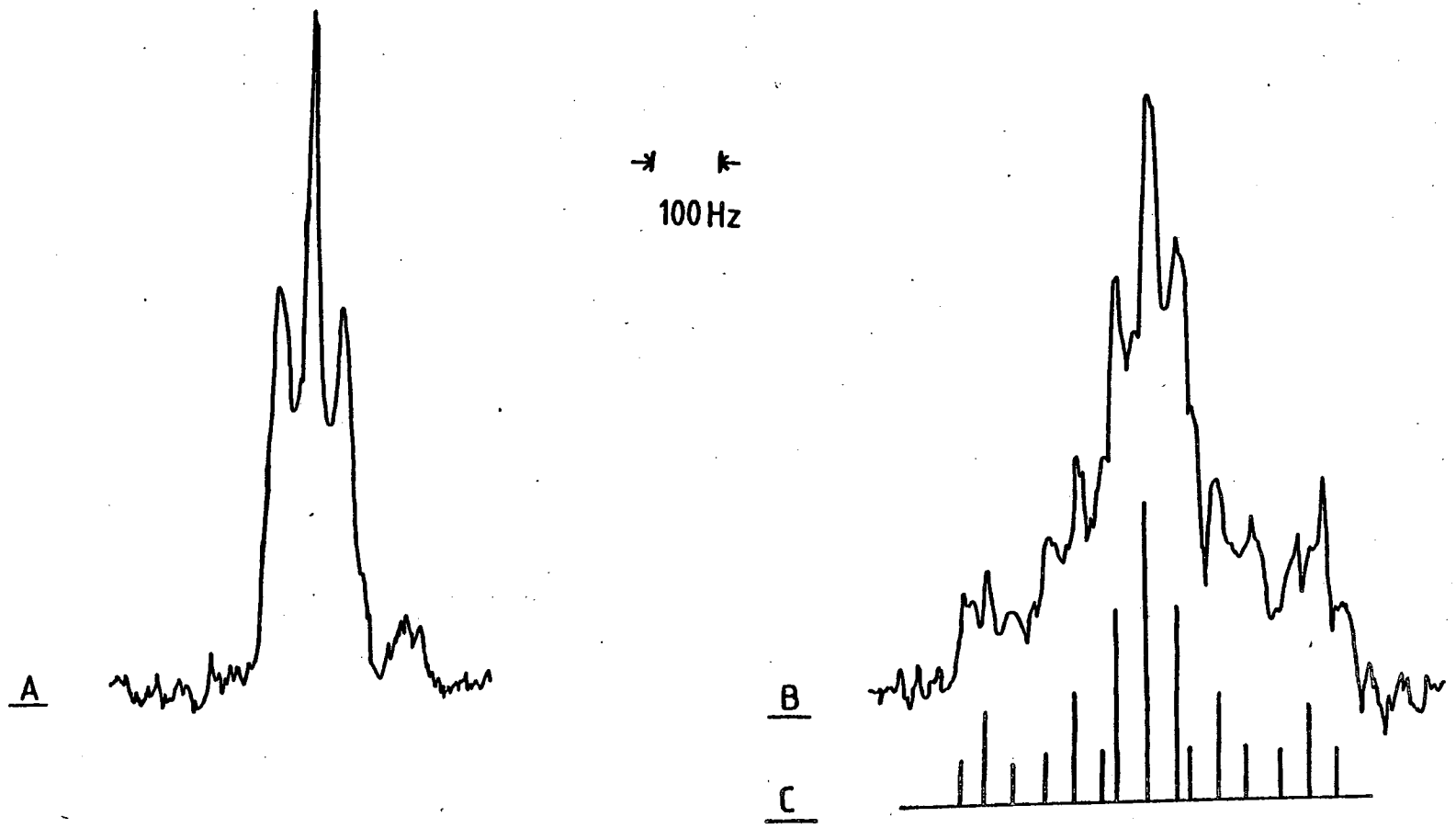
cont/d....

Table 4:1 cont/d..

Notes: a. From reference 83 unless stated otherwise, other parameters, $\delta^{1}H'$ = +7.19 ppm, $^{1}J(^{15}NH)$ = -73.1 Hz, $^{2}J_{PH'}$ = +18.8 Hz, $^{3}J_{HH'}$ = +3.1 Hz, $^{3}J_{FH'}$ = +8.0 Hz.

b. Measured in the course of this work in $CDCl_3$-$SiMe_4$ (3:1) at 223 K.

Figure 4:1 The central multiplets from the ^{31}P n.m.r. spectra, showing the resolution of $^{1}J(P^{14}N)$.
a) $PF_2[N(SiH_3)_2]$, b) $N(PF_2)_2(SiH_3)$, c) stick diagram of b) showing the five triplets due to second order effects.



resultant second order ^{19}F and ^{31}P spectra were analysed in the same way as those of the germyl analogue[95,96]. Double resonance experiments on $PF_2[^{15}N(SiH_3)_2]$ enabled $\delta^{15}N$ and signs of coupling constants (relative to $^1K_{PF}$, assumed to be negative) to be determined. Table 4:1 summarises the parameters recorded.

Chemical Shifts

The ^{31}P, ^{19}F and ^1H chemical shifts of $PF_2[^{15}N(SiH_3)_2]$ and $^{15}N(PF_2)_2(SiH_3)$ are unexceptional, coming in the regions usually associated with such compounds[31,36,83], and are very helpful in confirming their identities. Substitution of SiH_3 groups for protons in the series $PF_2(NH_2)$, $PF_2[NH(SiH_3)_2]$ and $PF_2[N(SiH_3)_2]$; and $NH(PF_2)_2$ and $N(PF_2)_2(SiH_3)$ produces a high frequency shift in δP of ca. 5 p.p.m., and δF increases in the first series by ca. 4 p.p.m. but only 1 p.p.m. in the second series. Similar changes were noted for the germyl analogues. For the first series, δSiH increases with the electronegativity of the other substituents on the nitrogen, but for $^{15}N(PF_2)_2(SiH_3)$ δH is actually lower than the other compounds even though there are two PF_2 groups in this molecule. Replacement of amino protons in $PF_2(NH_2)$ by SiH_3 groups produced low frequency shifts of $\delta^{15}N$. The same effect was noted for the germyl analogues, and other silyl amines[83].

Coupling Constants

All the spectra showed the expected multiplicities due to coupling with all the other magnetic nuclei present, and ^{29}Si satellites were distinguishable in $\{^1H\}$ or $\{^{15}N\}$ decoupled ^{31}P, ^{19}F and ^1H spectra. Although the cause of these satellites could not be endorsed by triple resonance experiments due to the limited

equipment available, double resonance experiments confirmed all the other couplings.

The signs and, generally, the magnitudes of the various couplings in $PF_2[^{15}N(SiH_3)_2]$ are the same as those found for $PF_2[^{15}NH(SiH_3)]$[83] and $PF_2[^{15}N(GeH_3)_2]$, implying similar bonding characteristics in silyl and germyl amines. Again, the positive value of $^4J_{FH}$ implies through-space interactions between the coupled nuclei. The signs of the couplings specified for $^{15}N(PF_2)_2(SiH_3)$ were deduced from the analysis of the spectra - double resonance experiments to determine the other couplings' signs were not performed - and $^3J_{PF}$, is of opposite sign to $^1J_{PF}$, as usually happens in $X(PF_2)_2$ compounds[97,121].

As expected for a P^{III} compound[117,118,119,120], $^1J(P^{15}N)$ is positive for $PF_2[^{15}N(SiH_3)_2]$. An unusual feature of the ^{31}P spectra of both silyl amines is that $^1J(P^{14}N)$ is resolvable, Figure 4:1, with the resonances resembling a 2:3:2 triplet due to overlap of the broad lines. Using the formula $^1J(P^{14}N) = 0.7129\ ^1J(P^{15}N)$ gives quite acceptable calculated couplings compared to the measured values. Resolution of $^1J(P^{14}N)$ implies that the electric field gradient at the nitrogen is rather small.

Albright and Gray[119,120] have recently suggested that $^1J(P^{15}N)$ should increase with increasing electronegativity of the substituents on the phosphorus, and with increasingly bulky groups on the nitrogen, or any other groups which would tend to make it planar. However comparison of the entire germyl and silyl series of compounds, and their parent amines[35,83], and $PCl_2(NMe_2)$[120] does not reveal any consistent trends which support these ideas. Indeed these authors supply some contradictory evidence as well, to try and support their CNDO/FPT2 calculations. Subtle changes in $^1J(P^{15}N)$ obviously require careful thought.

Comparing the complete series of silyl and germyl amines, it is clear that $^1J_{PF}$ increases with increasing electronegativity of substituents on the nitrogen.

It was suggested in Chapter 3 that the orientation of the phosphorus lone pair was crucial in determining the value of some two- and three-bond couplings to ^{31}P, with large couplings observed to nuclei cis to the lone-pair. The fairly large $^3J_{PH}$ = 9.3 Hz in $PF_2[N(SiH_3)_2]$ results from fast rotation about the P-N bond giving a weighted average of a large and a small coupling, as in $PF_2[N(GeH_3)_2]$; while in $N(PF_2)_2(SiH_3)$, as with $N(GeH_3)(PF_2)_2$, the conformation most likely to be adopted is that of Figure 4.2, with the lone pairs trans to the protons, giving the small $^3J_{PH}$ = 3.5 Hz.

The orientation of the lone pairs also affects $^2J(P^{29}Si)$; $^2J(P^{29}Si)$ is substantially larger (25 Hz) in $PF_2[N(SiH_3)_2]$ than in $N(PF_2)_2(SiH_3)$ (7Hz) for the same reasons as $^3J_{PH}$. There are very few other examples of $^2J(P^{29}Si)$ for comparison, but after completion of this work, Keat[109] reported some $^2J(P^{29}Si)$'s and came to similar conclusions about the effect of the P lone pair. The same reasoning has been applied to $PCl(Ph)(NMe_2)$ and $PPh(OMe)(NMe_2)$ where both molecules[105] have two different $^2J(P^{13}C)$'s (at 213 K and 173 K respectively). For $PF_2[N(SiH_3)_2]$ also, very low temperature spectra might sufficiently slow up rotation about the P-N bond to resolve two $^2J(P^{29}Si)$'s and $^3J_{PH}$'s.

These are the only compounds for which $^3J(^{29}SiF)$ has been reported. The smallish values are probably due to the number of intervening bonds. The greater value found for $N(PF_2)_2(SiH_3)$ compared with $PF_2[N(SiH_3)_2]$ can be associated with a greater through-space contribution in $N(PF_2)_2(SiH_3)$ via F--H interactions due to the expected orientations of the fluorines. In $PF_2[N(SiH_3)_2]$ only one silicon at a time can

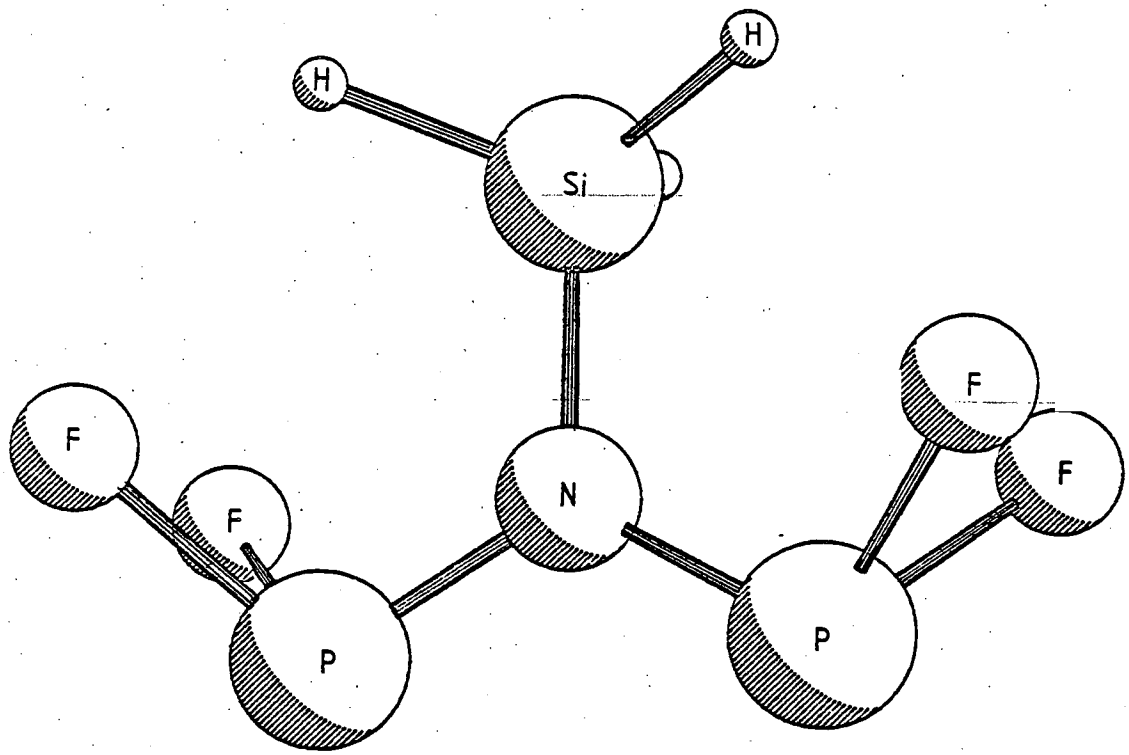


Figure 4:2 Proposed structure of $N(PF_2)_2(SiH_3)$.

Table 4:2

Variable Temperature ^{19}F N.m.r. Study[a] of $^{15}N(PF_2)_2(SiH_3)$

Temperature (K)	$^2J_{PP'}$ (Hz)
203	397.0
233	375.6
263	354.2
293	333.2

Other Parameters	293 K	203 K
$^1J_{PF}$	-1257.9 Hz	-1252.9 Hz
$^2J(F^{15}N)$	no change[b]	
$^3J_{PF'}$	+27.8 Hz	+22.8 Hz
$^4J_{FF'}$	no change[b]	
$^4J_{FF''}$	no change[b]	
$\delta^{19}F$	-61.4 ppm	-62.4 ppm

Solvent: $CDCl_3$/TMS//3/1

Notes: a. This study was made at a later date than the initial characterisation of the compound (Table 4:1) and the temperature calibration is not exactly comparable between the two tables.

b. Within experimental error, which was ±0.5 Hz for these couplings, ±0.1 Hz for the other parameters.

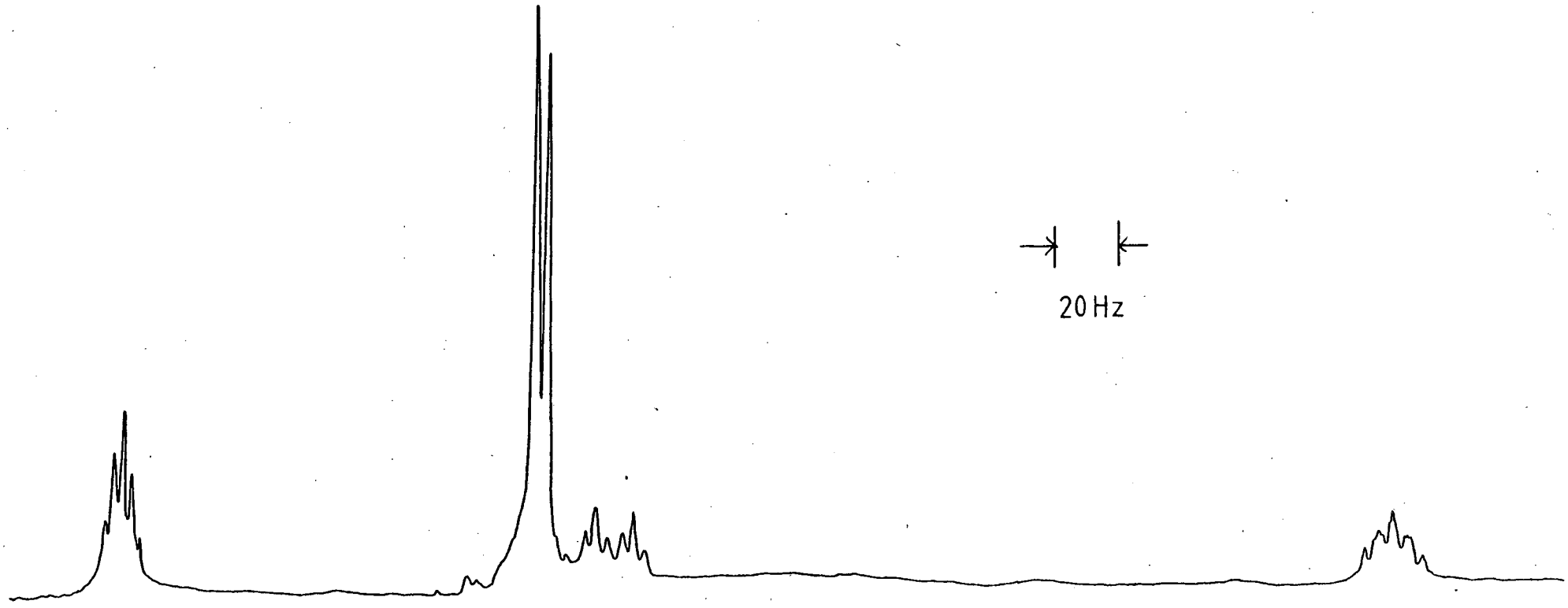


Figure 4:3 A. ^{19}F n.m.r., high frequency half, of $^{15}N(PF_2)_2(SiH_3)$, ^{1}H decoupled, at 213K.

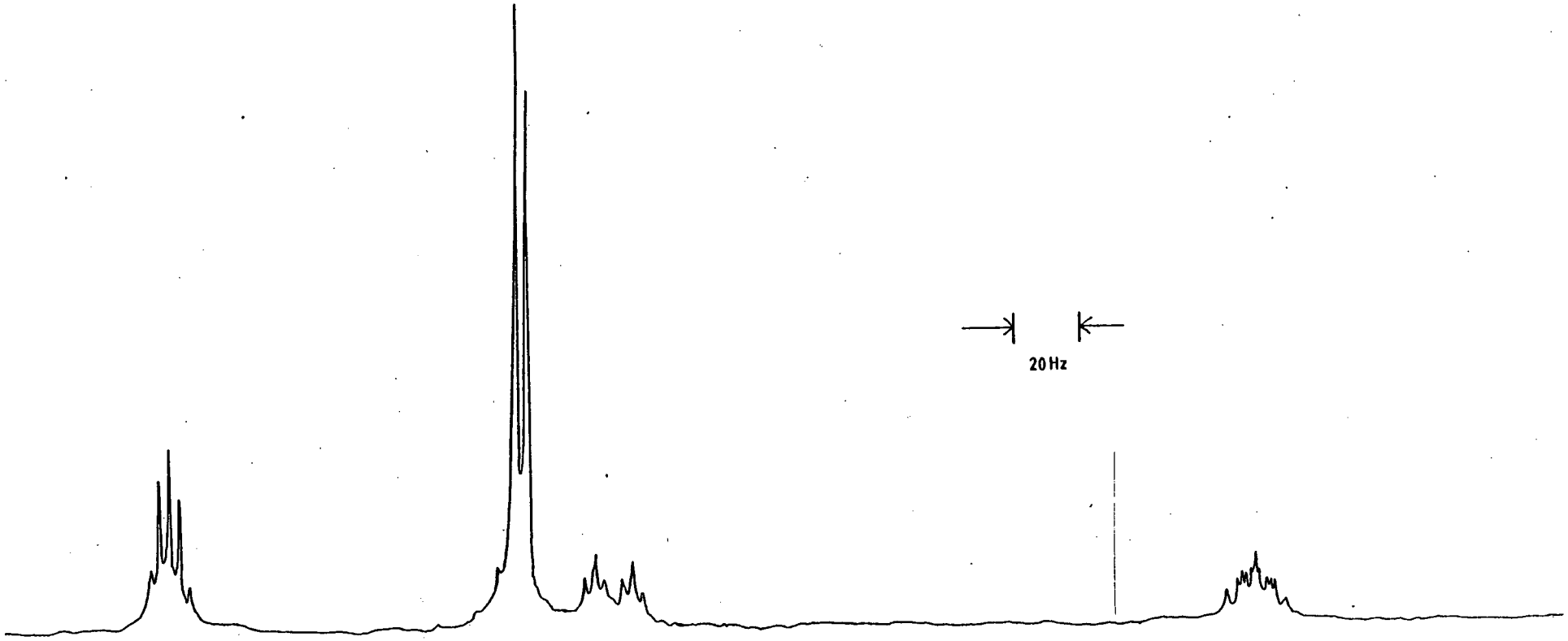
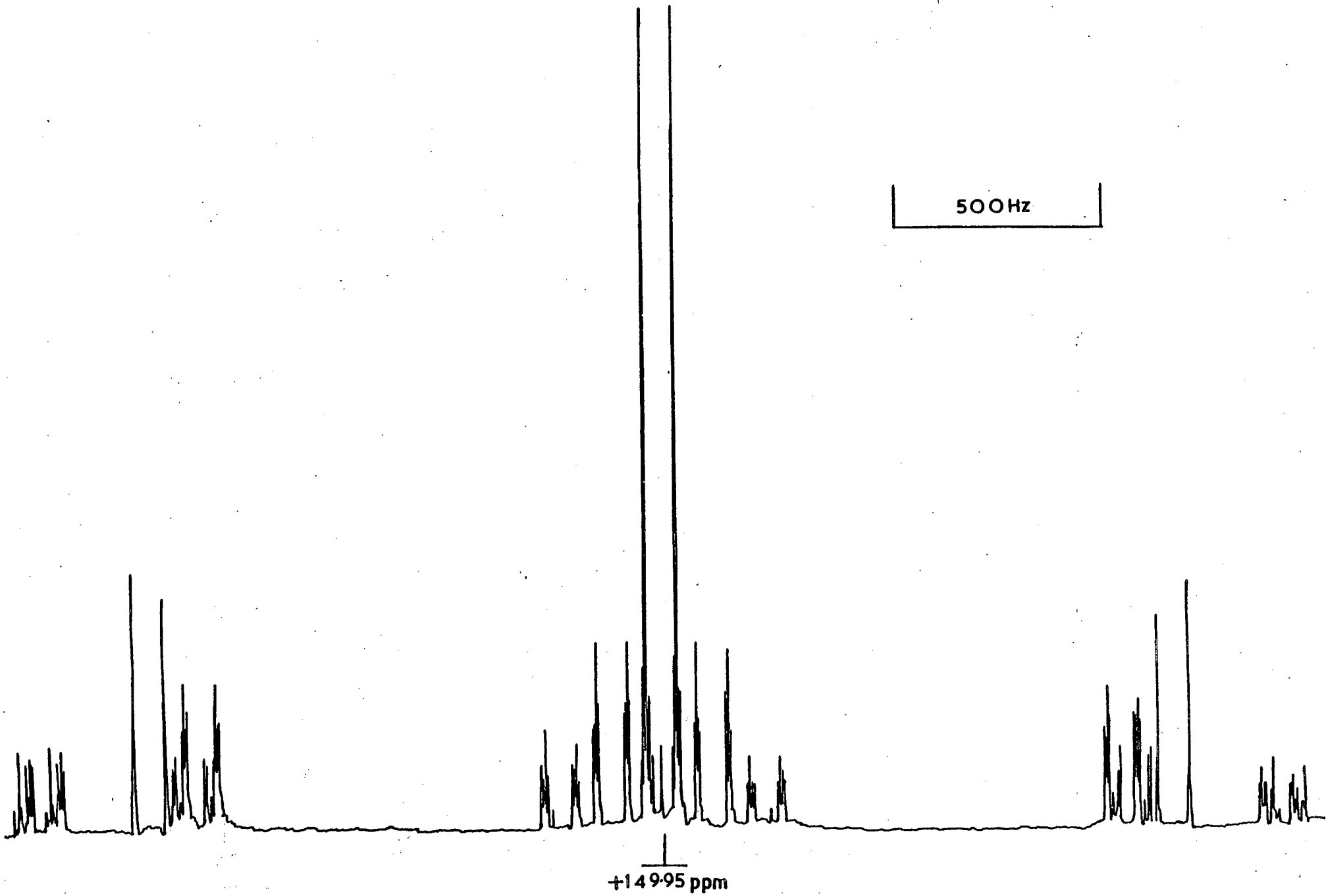


Figure 4:3 B. ^{19}F n.m.r., high frequency half, of $^{15}N(PF_2)_2(SiH_3)$, ^{1}H decoupled, at 303K.

Figure 4:3 C. ^{31}P n.m.r., ^{1}H decoupled, of $^{15}N(PF_2)_2(SiH_3)$, showing the complex second order features.



benefit from such interactions, and at very low temperatures two different $^{3}J(^{29}SiF)$'s might be resolved if the molecule assumed a conformation with the fluorines near one of the SiH_3 groups.

In Chapter 3, $^{2}J_{PP}$ in $N(GeH_3)(PF_2)_2$ was discussed in terms of an interaction between the phosphorus lone pairs. As $N(PF_2)_2(SiH_3)$ will have a similar conformation to $N(GeH_3)(PF_2)_2$, clearly $^{2}J_{PP}$ will be of a similar magnitude. However, the less sterically demanding SiH_3 group will allow a widening of the PNP angle, reducing the interaction, and thus accounting for the silyl compound's smaller coupling.

Variable Temperature N.M.R. Study of $^{15}N(PF_2)_2(SiH_3)$

As with $N(GeH_3)(PF_2)_2$, the ^{19}F n.m.r. spectrum of $N(PF_2)_2(SiH_3)$ is temperature dependant - Table 4:2. Although 5Hz is an insignificant change in $^{1}J_{PF}$ over the 90 K range studied, it is equivalent to a 22% change in $^{3}J_{PF'}$. This might be due to increased torsions about the P-N bond. But strangely enough $^{4}J_{FF'}$ and $^{4}J_{FF''}$ show no change (within experimental error) over the 90 K range yet these are often subject to large variations[121] due to P-N torsions. Unfortunately the significance of possible changes in $^{3}J_{PH}$ were not realised at the time, and not studied. The very large changes in $^{2}J_{PP}$ noted for $N(GeH_3)(PF_2)_2$ occurred here too - from 333.2 Hz at 293 K to 397.0 Hz at 203 K, and the same explanation as in Chapter 3 - increased P-N torsions as the temperature is raised decreasing the lone pair interactions, and hence the coupling - applies here too.

4:4 Infra-Red Spectra

The i.r. spectra of these two compounds, listed in Table 4:3, are not very difficult to interpret in terms of group frequencies,

Table 4:3

Infra-Red Spectra (cm^{-1})

$PF_2[N(SiH_3)_2]$		$N(PF_2)_2(SiH_3)$		
Gas	Solid	Gas	Solid	Assignment
2212)s,sh 2189)s	2185 s	2220 ms	2230 m) 2218 m) 2199 m) 2178 m)	νSiH_3
1930 vw 1900 vw		1946 vw 1907 vw		2 x ~965
		1638 vw		
1014 m	1034 s		)	ν skeletal
1004 m	1000 mw		992 m)	(νPN, ν_{as}PNP,
990)s,sh	958 s	963)vs	964 s)	$\nu_s Si_2N$)
970)s	927 s	954)	935)sh)	
			918)vs)	
926 vs	893 vs	936 vs	886)sh)	δSiH_3
822)s,sh			838 m)	
815)s	819 m	830 vs	814 s)	νPF_2
808)	791 s	817 vs	790)vs)	
795 s			774)sh)	
734 mw	751)s	751 w	736 m)	ρSiH_3
	730)s,sh	713 w	705 w)	
674 w	685 w	656 w	660 w)	ν skeletal
529 w	532)w	548 w		(ν SiN ?
	523)			$\nu_a Si_2N$?)
			478 w	
		465 m	462 m	
			447 w	δPF_2
			431 w	
			408 w	
368)w	357 m	362)m	367 s)	δ or ω PF_2
362)		348)sh	357 m)	
325 mw	326)m	291)	)	ω or ρ PF_2
	319)w,sh	282)w	)	

although some assignments are only tentative, for the molecules must have low symmetry and mixing of vibrations, especially those of the PF_2 groups with the so-called "skeletal" modes, will be considerable. There are bands in the regions usually associated with stretching and deformation modes of SiH_3[36,44] and PF_2 groups[24,32,35,36], which help confirm the compounds identities, and generally the spectra are similar in appearance to those of the germyl analogues, with the exception that modes involving a silicon atom are at higher frequency, due to its lower mass. In alkyl analogues of these compounds, a band at $\sim$1000 cm^{-1} is often assigned[24,34,35,90,91] to νCN, but the same band appears in these silyl (and the germyl) compounds and is assigned to a P-N stretching mode.

4:5 Photoelectron Spectra

The assignments of bands in the P.E. spectra of both amines, shown in Figure 4:4 and Table 4:4, were relatively straightforward and followed quite closely those of the germyl analogues. The nitrogen $2p_z$ and phosphorus $3p_z$ lone pairs were, as usual[35,84], assigned to the lowest and second lowest energy levels respectively. The next lowest energy bands, at similar I.P.'s to other silyl amines[36,84,138], are the Si-Hσ and Si-Nσ levels. The almost characteristic broad band at ca. 15.3 eV is again assigned to the P-Nσ bond, while the overlapping highest energy bands are the F $2p_\pi$ and P-Fσ levels. All the bands were devoid of vibrational fine structure.

Replacing protons in the parent amines[35,84] with MH_3 groups[138] causes a reduction in the N $2p_z$ and P $3p_z$ I.P.'s, the magnitude of these reductions being in the order $CH_3 > GeH_3 > SiH_3$.

Table 4:4

Photoelectron Spectra

$PF_2[N(SiH_3)_2]$	$N(PF_2)_2(SiH_3)$	Assignment
eV	eV	
10.75		$N2p_z$, $P3p_z$
	11.2	$N2p_z$
	11.7)	
	)	2 x $P3p_z$
	12.15)	
12.25)	13.45	SiHσ
)		
12.7)		
13.65	14.25	SiNσ
15.15	15.55	PNσ
	16.05)	
	)	$F2p_\pi$
16.7[a]	16.75[a])	
	17.5[a])	
	)	PFσ
17.75	18.4)	

Note:- a. These bands possibly include the Si3s level.

Table 4:5

Photoelectron Spectra of Some Amines

Amine	Assignments (eV)		Reference
	$N2p_z$	$P3p_z$	
$N(CH_3)_3$	8.5		138
$N(GeH_3)_3$	9.2		138
$N(SiH_3)_3$	9.7		138
$PF_2[N(CH_3)_2]$	9.6	10.5	84
$PF_2[N(GeH_3)_2]$	10.5	11.3	this work
$PF_2[N(SiH_3)_2]$	10.75	10.75	this work
$N(CH_3)(PF_2)_2$	?	?	
$N(GeH_3)(PF_2)_2$	10.75	11.0, 11.6	this work
$N(PF_2)_2(SiH_3)$	11.2	11.7 12.15	this work
$N(CH_3)_2(SiH_3)$	8.5		138
$N(CH_3)(SiH_3)_2$	9.2		138
$PF_2(NH_2)$	10.9	11.5	84
$NH(PF_2)_2$	11.3	11.9, 12.3	35
$N(PF_2)_3$	11.2	12.2, 12.5	35

Figure 4:4 A. Photoelectron spectrum of $PF_2[N(SiH_3)_2]$.

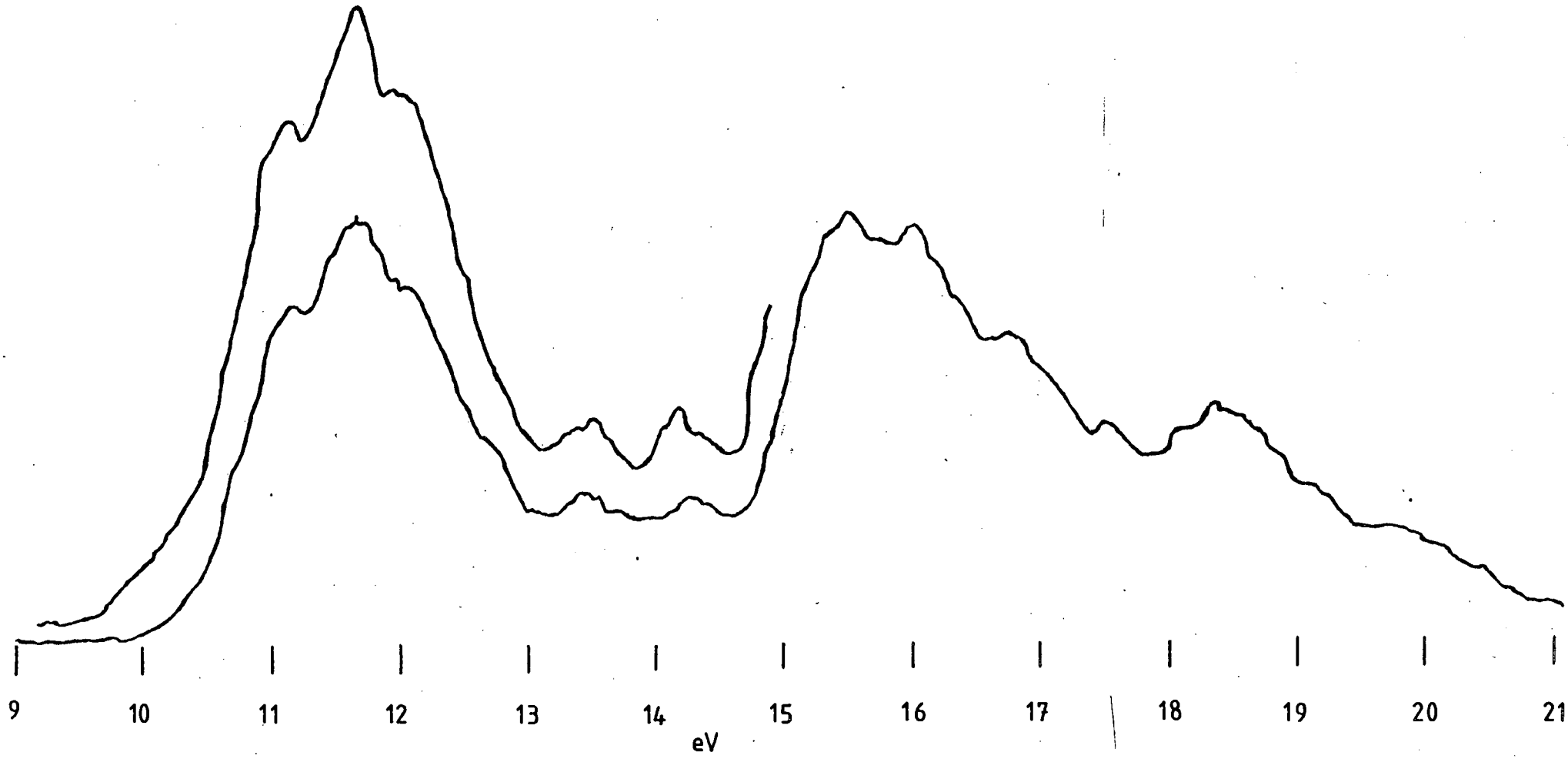


Figure 4:4 B. Photoelectron spectrum of $N(PF_2)_2(SiH_3)$.

Substitution of a PF_2 group for an H or MH_3 group in an amine raises the N $2p_z$ level - Table 4:5 - and while the group's electronegativity contributes something to this, it has also been suggested as partly due to $p\pi \rightarrow d\pi$ bonding[138].

Many papers[44] have dealt with the possibility of $p\pi \rightarrow d\pi$ bonding in phosphorus, germanium and silicon compounds. If the nitrogen lone pair has some bonding properties then a higher I.P. would be expected than that observed in molecules where this π-type interaction is likely to be absent or much reduced. Comparisons by Cradock et al.[138] of a series of amines showed consistently higher I.P.'s for the N $2p_z$ electrons of silyl amines than methyl amines, with $N(GeH_3)_3$ occupying an intermediate position. This was interpreted as supporting $(p \rightarrow d)\pi$ bonding in silyl and germyl amines, even though these P.E. spectra could not be as fully analysed as those of the MH_3 (M = C, Ge, Si) derivatives of Group VI and VII elements which also supported this belief[139,140,141]. Also, Cradock did not find the shape of the broad lone pair bands reconcilable with the expected sharpness of a non-bonding pair's band.

Comparison of the silyl and germyl amines studied here with their methyl equivalent shows an order of nitrogen lone pair I.P.'s identical to that previously reported viz. Si>Ge>C, implying this is the order of effectiveness of $(p \rightarrow d)\pi$ bonding. If π bonding was absent, electronegativity considerations would suggest the exact opposite order of I.P.'s, the less electronegative SiH_3 not binding the lone pair as tightly as the CH_3 group. An e.d. study[143] of $PF_2[N(SiH_3)_2]$ implied a planar skeleton which also suggests π bonding, and other e.d., basicity, i.r. and Raman studies of other molecules gave the same order of π bonding ability.[43,44]

As the N and P lone pair levels of $PF_2[N(SiH_3)_2]$ overlap it is concluded that the axes of the two lone pairs must be orthogonal. As $N(PF_2)_2(SiH_3)$ has approximately C_{2v} symmetry, the two P lone pairs (and the N lone pair) have a_1 and b_1 (and b_2) symmetry and so the overlap of these levels is possible and does not invalidate the suggestion that a physical interaction between the P lone pairs is responsible for the large, temperature dependent, $^2J_{PP}$ observed.

4:6 Mass Spectra

It proved necessary to purge the spectrometer with SiH_3Br before recording the spectra of these amines to ensure that hydrolysis products were not the main features observed. Both spectra were reasonably easy to interpret.

$PF_2[N(SiH_3)_2]$

The parent ion is quite prominent - Table 4:6 - and there are two main fragmentation pathways. The first involves loss of an SiH_3 group, followed either by HF or the second SiH_3 group, the former being preferred at high ionising voltages, the latter at low ionising voltages. The other route is via loss of PF_2 followed by loss of an SiH_3 group, but this is the less favoured of the two routes. Gain and loss of protons also occurred.

Also present were $[NH(SiH_3)_2]^+$ and $[NH_2(SiH_3)]^+$, and fragments containing Si atoms were seen to lose each proton until only the bare skeleton remained. The appreciable presence and therefore implied stability of ions such as $[NSi_2]^+$, $[SiN]^+$, $[FPNSi]^+$ and $[SiNP]^+$ may be due to the stabilising influence of $(p\rightarrow d)\pi$ bonding. No metastable ions were observed.

Table 4:6

Mass Spectrum of $PF_2[N(SiH_3)_2]$

m/e	Relative Abundance at 70 eV	Relative Abundance at 17 eV	Ion
147	3.7	7.1	^{30}Si, $^{29}Si + ^{15}N$
146	5.6	8.9	^{29}Si, ^{15}N
145	5.9	100	$[PF_2\{N(SiH_3)_2\}]^+$
116	3.7		^{29}Si, ^{15}N
115	20	20.5	$[PF_2\{NH(SiH_3)\}]^+$
114	100	11	$[PF_2(NSiH_3)]^+$
113	85	42	$[PF_2(NSiH_2)]^+$
112	59		$[PF_2(NSiH)]^+$
111	2.7		$[PF_2(NSi)]^+$
96	3.7		$[PF\{NH(SiH_3)\}]^+$
95	3.2		$[PF(NSiH_3)]^+$
94	56		$[PF(NSiH_2)]^+$
93	7.4		$[PF(NSiH)]^+$
92	18		$[PF(NSi)]^+$
85	2.1	4.5	$[PF_2(NH_2)]^+$
79	2.8		^{30}Si, $^{29}Si + ^{15}N$
78	21.5	10	$[O(SiH_3)_2]^+$, ^{29}Si, ^{15}N
77	34	1.3	$[NH(SiH_3)_2]^+$ $[P\{NH(SiH_3)\}]^+$
76	56	1.3	$[N(SiH_3)_2]^+$ $[P(NSiH_3)]^+$
75	27		$[N(SiH_3)(SiH_2)]^+$ $[P(NSiH_2)]^+$
74	19		$[N(SiH_2)_2]^+$ $[P(NSiH)]^+$
73	20.5		$[N(SiH_2)(SiH)]^+$ $[P(NSi)]^+$
72	17.5		$[N(SiH)_2]^+$
71	4.6		$[N(SiH)(Si)]^+$
70	25		$[N(Si)_2]^+$
69	33		$[PF_2]^+$

Table 4:6 cont/d...

m/e	Relative Abundance at 70 eV	at 17 eV	Ion
67	4.5		$[PF(NH_3)]^+$
66	6.5		$[PF(NH_2)]^+$
65	4.5		$[PF(NH)]$
50	4		$[SiFH_3]^+$ $[PF]^+$
49	22		$[SiFH_2]^+$
48	8		$[SiFH]^+$
47	22.5	0.5	$[SiF]^+$ $[NH_2(SiH_3)]^+$
46	59	7	$[NH(SiH_3)]^+$ $[PNH]^+$
45	15	1	$[NSiH_3]^+$ $[PN]^+$
44	4		$[NSiH_2]^+$
43	2		$[NSiH]^+$
42	9		$[NSi]^+$
39	0.7		$[O(SiH_3)_2]^{++}$, ^{29}Si, ^{15}N
38.5	0.1		$[NH(SiH_3)_2]^{++}$ $[P\{NH(SiH_3)\}]^{++}$
38	0.6		$[N(SiH_3)_2]^{++}$ $[P(NSiH_3)]^{++}$
37.5	0.3		$[N(SiH_3)(SiH_2)]^{++}$ $[P(NSiH_2)]^{++}$
37	1.4		$[N(SiH_2)_2]^{++}$ $[P(NSiH)]^{++}$
36.5	0.6		$[N(SiH_2)(SiH)]^{++}$ $[P(NSi)]^{++}$
36	1.2		$[N(SiH)_2]^{++}$
35.5	0.1		$[N(SiH)(Si)]^{++}$
35	0.3		$[NSi_2]^+$
32	1.4		$[SiH_4]^+$
31	10		$[SiH_3]^+$
30	3.4		$[SiH_2]^+$
29	8.5		$[SiH]^+$
28	8		$[Si]^+$

Exact Mass: Theoretical 144.974448
Observed 144.974594
Error <2 ppm

Table 4:7

Mass Spectrum of $N(PF_2)_2(SiH_3)$

m/e	Relative Abundance	Ion
183	0.2	$[N(PF_2)_2(SiH_3)]^+$
154	0.9	$[NH_2(PF_2)_2]^+$, ^{15}N
153	73	$[NH(PF_2)_2]^+$
152	41	$[N(PF_2)_2]^+$
134	10	$[NH(PF_2)(PF)]^+$
133	31	$[N(PF_2)(PF)]^+$
116	1.2	^{30}Si, ^{15}N + ^{29}Si
115	1.5	$[NH(PF_2)(SiH_3)]^+$, ^{15}N, ^{29}Si
114	24	$[N(PF_2)(SiH_3)]^+$, $[N(PF_2)(P)]^+$
113	0.8	$[N(PF_2)(SiH_2)]^+$
112	8.5	$[N(PF_2)(SiH)]^+$
111	1.5	$[N(PF_2)(Si)]^+$
96	0.6	$[NH(PF)(SiH_3)]^+$
95	1.2	$[N(PF)(SiH_3)]^+$, $[N(PF)(P)]^+$
94	2.2	$[N(PF)(SiH_2)]^+$
93	0.5	$[N(PF)(SiH)]^+$
92	0.6	$[N(PF)(Si)]^+$
88	6	$[PF_3]^+$
86	1.5	$[PF_2(NH_3)]^+$, ^{15}N
85	9	$[PF_2(NH_2)]^+$
84	4.5	$[PF_2(NH)]^+$
79	4	^{30}Si, ^{29}Si + ^{15}N, ^{29}Si
78	7	$[O(SiH_3)_2]^+$, ^{29}Si, ^{15}N
77	60	$[NH(SiH_3)_2]^+$
76	24	$[N(SiH_3)_2]^+$ $[P(NSiH_3)]^+$ $[N(P)_2]^+$
75	33	$[N(SiH_3)(SiH_2)]^+$ $[P(NSiH_2)]^+$

Table 4:7 cont/d..

m/e	Relative Abundance	Ion
74	5	$[N(SiH_2)_2]^+$ $[P(NSiH)]^+$
73	15	$[N(SiH_2)(SiH)]^+$ $[P(NSi)]^+$
72	6.5	$[N(SiH)_2]^+$
69	100	$[PF_2]^+$
67	2.5	$[PF(NH_3)]^+$
66	2.5	$[PF(NH_2)]^+$ ^{15}N
65	66	$[PF(NH)]^+$
64	3	$[PF(N)]^+$
50	8	$[SiFH_3]^+$, $[PF]^+$
49	23	$[SiFH_2]^+$
48	14	$[SiFH]^+$
47.5	0.3	$[N(PF)(SiH_3)]^{++}$, $[N(PF)(P)]^{++}$
47	7	$[SiF]^+$, $[NH_2(SiH_3)]^+$, $[O(SiH_3)]^+$
46	48	$[P(NH)]^+$ $[NH(SiH_3)]^+$
45	3.5	$[PN]^+$ $[N(SiH_3)]^+$
39	0.5	$[O(SiH_3)_2]^{++}$, ^{29}Si, ^{15}N
38.5	0.1	$[NH(SiH_3)_2]^{++}$
38	1.7	$[N(SiH_3)_2]^{++}$ $[P(NSiH_3)]^{++}$
37.5	1	$[N(SiH_3)(SiH_2)]^{++}$ $[P(NSiH_2)]^{++}$
37	3.5	$[N(SiH_2)_2]^{++}$ $[P(NSiH)]^{++}$
36.5	1.2	$[N(SiH_2)(SiH)]^{++}$ $[P(NSi)]^{++}$
36	3	$[N(SiH)_2]^{++}$
32	0.8	$[SiH_4]^+$, ^{29}Si
31	12	$[SiH_3]^+$
30	0.9	$[SiH_2]^+$
29	3	$[SiH]^+$
28	5	$[Si]^+$
20	1.5	$[HF]^+$

Metastable: m/e = 115.6, weak; $[NH(PF_2)_2]^+ \rightarrow [N(PF_2)(PF)]^+ + HF$

Exact Mass: Theoretical 182.944613
Observed 182.942775
Error <11 ppm

$\underline{N(PF_2)_2(SiH_3)}$

The parent ion was not particularly strong (Table 4:7), in spite of the stability of the compound itself, and the breakdown route is remarkably similar to that of $PF_2[N(SiH_3)_2]$. Loss of SiH_2 and SiH_3 gives $[NH(PF_2)_2]^+$ and $[N(PF_2)_2]^+$, followed by loss of F, HF (metastable observed), PF_2 or PF_3, the last named giving $[FPNH]^+$, an ion particularly readily formed in other systems too[32,35,36], such as $NH(PF_2)_2$ and $PF_2(NH_2)$. In the other main breakdown route, the parent ion loses PF_2 giving $[PF_2(NSiH_3)]^+$ followed either by loss of SiH_2F giving $[PF(NH)]^+$, or loss of F_2 leading to $[P(NSiH_3)]^+$.

Note that for both compounds the loss of H_2 seems to be preferred to simply losing H from the silyl group(s). This has been noted before in SiH_3 and GeH_3 species[144].

4:7 Reactions

Reaction with HBr

When equimolar amounts of $N(PF_2)_2(SiH_3)$ and HBr were allowed to react in an n.m.r. tube, the products were PF_2Br, SiH_3Br, a white solid assumed to be NH_4Br, and unreacted amine. Cleavage of the Si-N bond would produce $NH(PF_2)_2$ but no trace of this was found and as $NH(PF_2)_2$ is immune to attack[35] by HBr, it follows that a P-N bond must have broken first to give $PF_2[NH(SiH_3)]$ which is known to react further[36].

Similarly, reaction of equimolar quantities of $PF_2[N(SiH_3)_2]$ and HBr gave PF_2Br and SiH_3Br in a ratio of ca. 2:1, with $HN(SiH_3)_2$ and unreacted tertiary amine also present. Here also the P-N bond appears to be cleaved preferentially.

Table 4:8

Sulphur and $PF_2[N(SiH_3)_2]$

Stage	Temperature (K)	Reaction Time (hrs)	Approximate % of proton n.m.r. signals	
			$PF_2[N(SiH_3)_2]$	SiH_3F[a]
1	290	0.5	~99	~1
2	353	3	95	5
3	353	4.5	90	10
4	358	16	50	50
5	363	8	25	75

Solvent:- $CDCl_3$

Note:- a. From the decomposition of $PF_2[N(SiH_3)_2]$

Reaction with Water and Air

Reaction of the two amines with traces of water as described in Experimental Section 4:7 was studied by i.r. and n.m.r. spectroscopy. Water and $PF_2[N(SiH_3)_2]$ reacted to give $PF_2[NH(SiH_3)]$, $PF_2(NH_2)$, PF_3, $O(PF_2)_2$, $O(SiH_3)_2$, SiH_4, SiH_3F and white solids assumed to be NH_4F, SiO_2 and PN polymers, while $N(PF_2)_2(SiH_3)$ gave the same products with $NH(PF_2)_2$ instead of $PF_2[NH(SiH_3)]$. In both cases the initial reaction is therefore cleavage of an Si-N bond.

Exposure of small quantities of the gaseous compounds to the atmosphere produced vivid flashes, sharp explosions and clouds of white smoke.

Sulphur and $PF_2[N(SiH_3)_2]$

Oxidative addition of sulphur to $PF_2(NMe_2)$ yields $PF_2(NMe_2)(S)$, but the reaction takes about 5 days at 420 K[145]. The analogous oxidation of $PF_2[N(SiH_3)_2]$ was attempted in an n.m.r. tube, the mixture being heated as described in Table 4:8 and Experimental Section 4:8, but decomposition of the amine occurred and no phosphorus V compounds were observed.

Reaction between $PF_2N(SiH_3)_2$ and PF_2Br

Arnold's studies[47] of the reaction of simple silyl amines with PF_2Br revealed that although SiH_3Br and orange solids were often formed, only $HN(SiH_3)_2$ actually yielded a $PF_2N\langle$ compound ($PF_2[NH(SiH_3)]$), and this reaction followed a similar path. Eventually, after 24 hours at 293 K, SiH_3Br accounted for 20% of the ^1H n.m.r. signals, but no evidence for the formation of $N(PF_2)_2(SiH_3)$ or $N(PF_2)_3$ could be found. Orange solids were deposited.

Arnold's explanation of the products being too sterically crowded does not ring true as all the possible products from that study, and this, have now been prepared. Rather, it is more likely that stabilisation of the amine by $(p\rightarrow d)\pi$ bonding makes the change in geometry necessary to form the usual reactive intermediate[43] for such cleavage reactions unfavourable.

It is possible, in view of the halogen exchange reactions of $PF_2(N(CH_3)_2)$ (Chapter 9), that exchange to form $PFBr[N(SiH_3)_2]$ occurs, which then, by elimination of SiH_3Br, polymerises to give the orange solid, as traces of PF_3 were noted, although this is not conclusive evidence.

Reaction of $PF_2[N(SiH_3)_2]$ with PF_5, and PF_3O

A rapid reaction, Experimental Section 4:10, occurred between PF_5 and $PF_2[N(SiH_3)_2]$ to give $PF_2(NPF_3)$, presumably via a substitution reaction, followed by elimination of SiH_3F.

$$PF_2[N(SiH_3)_2] + PF_5 \rightarrow SiH_3F + [PF_2N(PF_4)(SiH_3)] \quad \ldots 4:3$$

$$[PF_2N(PF_4)(SiH_3)] \rightarrow SiH_3F + PF_2(NPF_3) \quad \ldots 4:4$$

[ ] = not observed

A similar reaction occurs[146] between $PF_2[N(SiMe_3)_2]$ and PF_5, and a reaction analogous to equation 4:3 has been observed for $PF_2[NH(SiH_3)]$ and PF_5 (Chapter 5). Hydrolysis of PF_5 to PF_3O took place, but as $PF_2[N(SiH_3)_2]$ and PF_3O were still both present after some time, it may be assumed that they do not react, as was also the case with $N(PF_2)_2(SiH_3)$ and PF_3O (Experimental Section 4:11).

Reaction of $N(PF_2)_2(SiH_3)$ with $Mo(CO)_4C_7H_8$

As explained in Experimental Section 4:12, there was no positive evidence for the formation of a complex between the amine and the molybdenum, but the amount of $N(PF_2)_2(SiH_3)$ present at the end of the reaction had clearly decreased, and it is possible that an insoluble product resulted from displacement of the norbornadiene. King has recently prepared[147,148,149] some interesting complexes of $N(CH_3)(PF_2)_2$ and transition metals, and these reactions should be investigated for the silyl compound in greater depth.

4:8 Reactions with Diborane

Reaction of a phosphine with diborane almost invariably leads to the formation of a BH_3 adduct[150,151], and these silyl amines were no exception. The adducts were extremely air sensitive, and solutions of them often spontaneously, and violently, burst into flames when exposed to the air - with the parent amines, the solutions merely fumed a lot. However the adducts were studied to different depths and it is best to discuss them separately.

a) $PF_2[N(SiH_3)_2]$

When $PF_2[N(SiH_3)_2]$ and B_2H_6 were warmed to room temperature in $CDCl_3$ in an n.m.r. tube, an immediate and quantitative reaction occurred, producing $H_3B.PF_2[N(SiH_3)_2]$, equation 4:5.

$$2\ PF_2[N(SiH_3)_2] + B_2H_6 \rightarrow 2\ H_3B.PF_2[N(SiH_3)_2] \quad \ldots 4:5$$

From the behaviour of the solution, it is likely that the product is a colourless liquid. Although not isolated, the product, which is fairly stable at 293 K, was unequivocally identified from n.m.r. spectra as as adduct with a BH_3 group co-ordinated to the phosphorus atom (BH_3 is known to prefer forming B-P rather than B-N bonds[151] and when

isolated, similar compounds, e.g. $H_3B.PF_2[NH(CH_3)]$, show B-P stretching frequencies in their i.r. spectra[91].

N.m.r. spectra

With ^{14}N species the spectra, ^{31}P in particular, were poorly resolved and ^{15}N labelling was essential to ensure positive identification of the compound. Broadening due to the quadrupolar ^{11}B also occurred. The parameters measured are listed in Table 4:9, and the spectra were all first order.

Chemical Shifts

Cowley[152] observed that, generally, $\delta B\underline{H}$ decreased as $^1J(P^{11}B)$ increased and this compound fits into his scheme quite well, having a smaller $^1J(P^{11}B)$ than $H_3B.PF_2(NMe_2)$ and a larger $\delta B\underline{H}$. In Cowley's interpretation, as electron donors decrease δH, then the more basic the phosphine, the more electrons are donated into the BH_3 moiety, causing a low frequency shift (while a stronger P-B bond would imply a larger $^1J(P^{11}B)$). However examination of $\delta B\underline{H}$ of adducts listed in order of basicity, after Lines and Centofanti[153], and Rudolf and Shultz[154], shows that these concepts break down, probably only being true within series of similar compounds[155] e.g. P-N compounds, or P-O compounds, but not for dissimilar sets of compounds e.g. a P-N and a P-O compound. It would seem therefore from $\delta B\underline{H}$ and $^1J(P^{11}B)$ that $PF_2[N(SiH_3)_2]$ is a weaker base than several $PF_2(NR_2)$ compounds[152]. Any $(p\rightarrow d)\pi$ bonding in alkyl compounds would only involve the P and the N implying a greater electron density on the phosphorus (and hence greater basicity) than in the silyl compound, where the N lone pair is also shared with two Si atoms. With the overall drift of electrons out to the BH_3 group, $\delta Si\underline{H}$ shifts to high frequency of the parent compounds.

Table 4:9

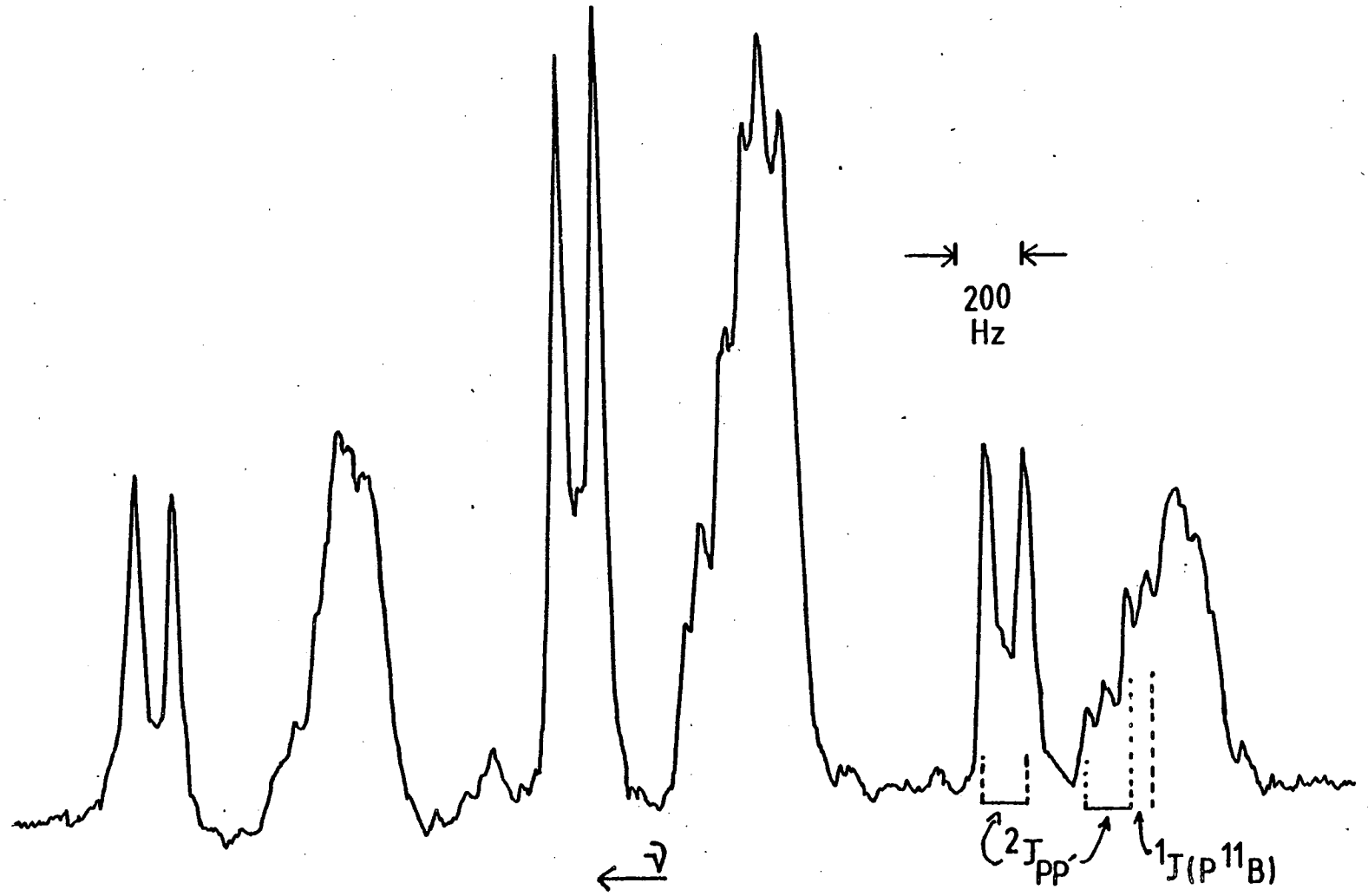
N.m.r. Parameters of the Borane Adducts

Parameter	$H_3B.PF_2[^{15}N(SiH_3')_2]$	$H_3B.PF_2[N(P'F_2')(SiH_3')]$	$N[PF_2(BH_3)]_2(SiH_3')$
δ^1H, ppm	0.78	n.o.[a]	n.o.[a]
δ^1H', ppm	4.47	n.o.[a]	n.o.[a]
$\delta^{19}F$, ppm	-60.2	-64.4	-60.7
$\delta^{19}F'$, ppm		-60.2	
$\delta^{31}P$, ppm	135.1	130.7±0.5	128.9±0.3
$\delta^{31}P'$, ppm		142.6	
$^1J_{PF}$ Hz	1209	1205±5	1250±5[b]
$^1J_{P'F'}$ Hz		1288	
$^1J(P^{15}N)$ Hz	40.9	n.s.	n.s.
$^1J(P^{11}B)$ Hz	72.4	55±0.5	n.o.[a]
$^1J(^{29}SiH)$ Hz	212	n.o.	n.o.
$^1J(^{11}BH)$ Hz	101	100±2	100±2
$^2J_{PH}$ Hz	16.0	n.o.	n.o.
$^2J(^{15}NH')$ Hz	4.2	n.s.	n.s.
$^2J(F^{15}N)$ Hz	n.o.		
$^2J_{PP'}$ Hz		118	<10
$^3J_{FH}$ Hz	16.0	17	16
$^3J_{PH'}$ Hz	6.9	n.o.	n.o.
$^4J_{FH'}$ Hz	2.1	n.o.	n.o.
$^5J_{HH'}$ Hz	n.o.	n.o.	n.o.
Solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$
Temperature (K)	303	223	223

Notes:- a. Not resolved; see text. b. $\left|{}^1J_{PF} + {}^3J_{PF'}\right|$; $^3J_{PF'}$ <5 Hz.

n.o. not observed n.s. not studied.

Figure 4:5 ^{31}P n.m.r. of $H_3B.\ PF_2[N(PF_2)(SiH_3)]$, showing $^2J_{pp}$ and $^1J(P^{11}B)$ (spectrum is partially overlapped with that of $N[PF_2(BH_3)]_2(SiH_3)$).



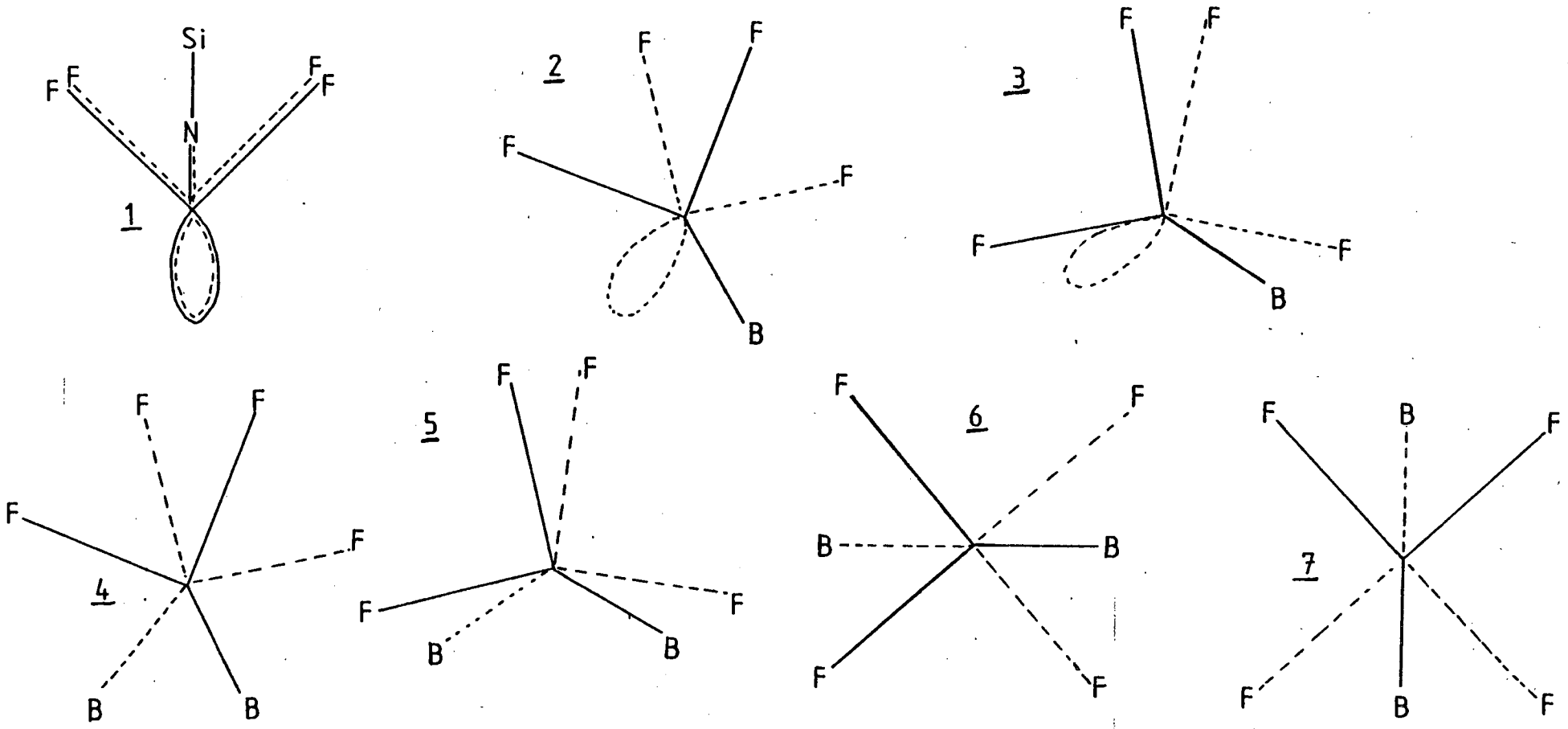


Figure 4:6 Possible structures of the BH_3 adducts to relieve steric congestion; 1 = $N(PF_2)_2(SiH_3)$; 2 and 3 = mono adduct; 4, 5, 6, and 7 = bis adduct. Only the PF_2 twist angles change from 1 through to 7, the N and SiH_3 are always in the same position.

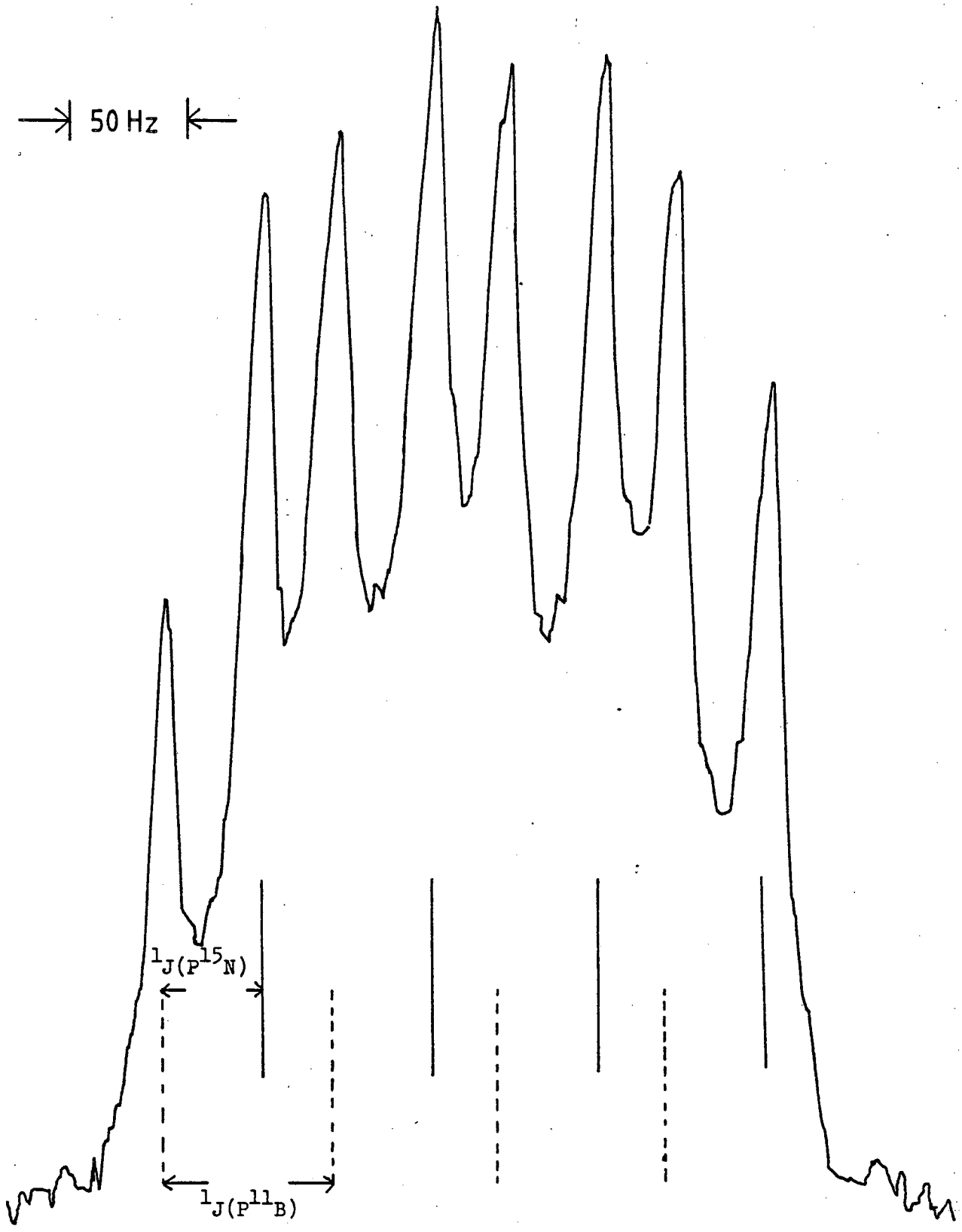


Figure 4:7 Central multiplet of ^{31}P n.m.r. of $H_3B.PF_2[^{15}N(SiH_3)_2]$, showing doublet of quartets from coupling with ^{15}N and ^{11}B.

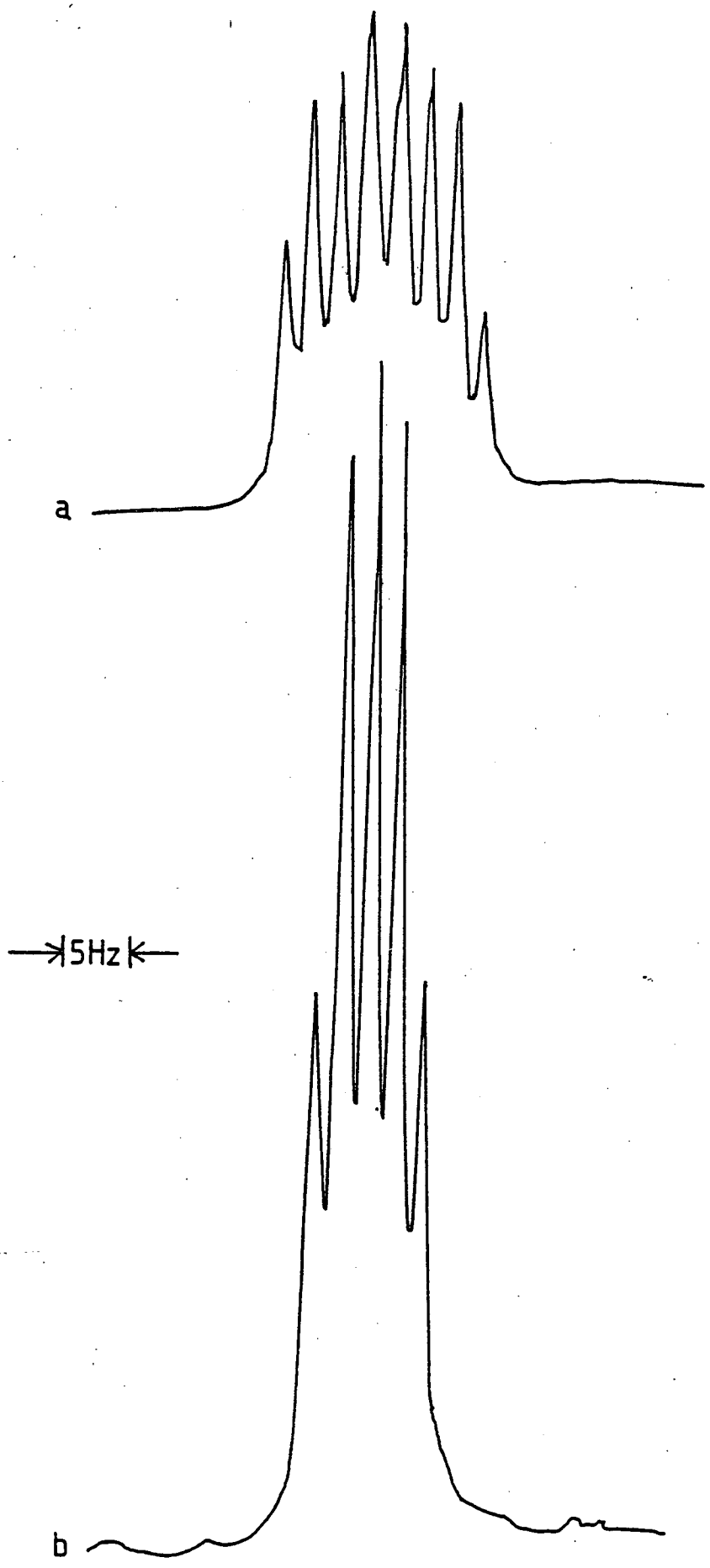


Figure 4:8 A. ^{1}H n.m.r. of SiH_3 region of $H_3B.PF_2[^{15}N(SiH_3)_2]$.

B. ^{31}P decoupled.

The large low frequency shift of δP is very good evidence for the formation of a B-P bond. A similar shift has been observed for all known BH_3 adducts of P-N compounds[31,152]. One usually associates electron withdrawing groups with high frequency shifts, but the paramagnetic term[62], not the diamagnetic term, dominates δP. A smaller low frequency shift of δF also occurs.

Coupling Constants

The coupling constants are generally consistent with those reported for related compounds[31,152,154], and the significance of the smallish value of $^1J(P^{11}B)$ (72 Hz as opposed to 79 Hz in $H_3B.PF_2[N(CH_3)_2]$) has already been discussed.

An increase in the phosphorus coordination number usually[31] results in a decrease in $^1J_{PF}$. As this is a four-coordinate P^{III}, the effect is not as great as in a four-coordinate P^V, and is further evidence of coordination to the phosphorus. Similar values to $^2J_{PH}$ and $^3J_{FH}$ here are found in adducts not containing nitrogen[152,155,156], which also confirms the B-P bond.

As mentioned in Chapter 3, $^1J(P^{15}N)$ decreases with increasing s-character in the P-N bond i.e. with increases in the phosphorus's coordination number. Although $^1J(P^{15}N)$ is markedly reduced upon adduct formation, the effect is not truly comparable with that of a four-coordinate P^V where the coupling is usually quite small[119,120]. As no negative coupling of this size has been found in a four-coordinate compound, it is felt that this coupling, the first $^1J(P^{15}N)$ reported for a borane adduct, is positive, like those of other P^{III} compounds[83].

The reduction in $^3J_{PH}$ upon adduct formation is consistent with the view that this coupling in $PF_2[N(SiH_3)_2]$ is a weighted

average due to the two possible orientations of the P lone pair, for with no lone pair in the adduct, the enhancement of the couplings to nuclei cis to it obviously cannot occur and therefore the average coupling is smaller.

b) $\underline{N(PF_2)_2(SiH_3)}$

The reaction of B_2H_6 with $N(PF_2)_2(SiH_3)$ - Experimental Section 4:14 - gives two products containing either one, or two BH_3 groups, and several n.m.r. tube reactions were carried out using either an excess of the amine or of B_2H_6. Spectra were recorded at 223 K after briefly warming the reactants to 290 K to initiate the reaction. Room temperature spectra were sometimes recorded to allow completion of the reaction. Neither of the two products was stable at 290 K.

The identification of the first adduct formed as the mono (borane) species, $H_3B.PF_2[N(PF_2)(SiH_3)]$, was simplified by the presence of two sets of ^{31}P resonances, both apparently first order, each coupled to two ^{19}F nuclei and to each other, with one set coupling to a ^{11}B nucleus, Figure 4:5. These points rule out the possibility of a bridging BH_3 group, or intramolecular exchange of the BH_3 group between the two phosphorus nuclei[156].

The ultimate product from all the reactions, even when excess amine was present, was easily identified as the bis (borane) adduct, $N[PF_2(BH_3)]_2(SiH_3)$, from the ^{31}P and ^{19}F spectra which both showed only one PF_2 environment, coupling to BH_3 groups, and were both centrosymmetric second-order patterns, as expected for an $X[PF_2(BH_3)]_2$ spin system.

Some systems with two PF_2 groups, e.g. P_2F_4[156], $O(PF_2)_2$[157], $S(PF_2)_2$[158] and $Se(PF_2)_2$[159] have only accepted one BH_3 group. This might be attributed to steric factors in the cases of P_2F_4, $S(PF_2)_2$

and $Se(PF_2)_2$, but the wide $\angle POP$[134] makes this seem less reasonable in the case of $O(PF_2)_2$. Some preliminary investigations of other $N(PF_2)_2$ compounds indicate that these too can coordinate two BH_3 groups[160].

N.m.r. spectra

The parameters recorded are listed in Table 4: 9. Samples were not labelled with ^{15}N. The ^{31}P spectrum of the mono adduct appeared to be first-order while the ^{31}P spectrum of the bis adduct as expected showed second-order features. Proton spectra showed SiH_3 and coordinated BH_3 groups but it was impossible to distinguish with certainty which of the complicated, overlapping, resonances were from which of the two species present in every sample.

The ^{19}F spectra were much more complicated than was anticipated from the ^{31}P spectra. The mono adduct showed second-order features (which were not fully analysed) implying that in each PF_2 group the fluorines were not magnetically equivalent which suggests that rotation about the P-N bonds is restricted. Unlike the parent amine, the second-order features of the bis species were very close together, as in $O(PF_2)_2$[121], and these too were not fully investigated.

Chemical Shifts

For both species, δP shifts to low frequency upon adduct formation, the uncomplexed phosphorus of the mono species being least affected while in the bis species the shift is greatest.

Only the complexed fluorines of the mono species shift to lower frequency, all the other fluorines move to higher frequency.

These different shifts might imply conformational changes, which is also suggested by the second-order nature of all these resonances. These adducts will be quite sterically congested, and any strain could be relieved by rotation about the P-N bonds, perhaps in opposite directions - Figure 4:6:3 - away from the structure of $N(PF_2)_2(SiH_3)$. This would clearly lead to magnetic (and perhaps even chemical) inequivalence of the four fluorines of the mono species, giving perhaps an AA'BB' spectrum, further complicated by long range P-F coupling. For the bis species a much greater rotation would clearly be necessary, perhaps a 180° turn by one of the PF_2 groups, or two 90° turns in opposite directions by both groups, Figure 4:6:6, which would place the BH_3 groups close to the other phosphorus fluorines and lead to F--H interactions, and this could make the fluorines inequivalent.

Coupling Constants

Significant reductions occur in $^2J_{PP'}$ upon complexation, changing from ca. 350 Hz in the free amine to 118 Hz in the mono adduct, to less than 10 Hz in the bis adduct. The large coupling in $N(PF_2)_2(SiH_3)$ was attributed to lone pair - lone pair interactions, and these reductions are fully consistent with this view, for such interactions will decrease as B-P bonds are formed. The suggested conformations will also contribute somewhat to reducing the interactions and the coupling.

The small $^1J(P^{11}B)$ = 55 Hz for the mono adduct implies that this phosphorus is significantly less basic than that in $PF_2[N(SiH_3)_2]$ and alkylaminodifluorophosphines[152]. Resolving this coupling means that the BH_3 group is not undergoing intramolecular exchange from phosphorus to phosphorus at 223 K, unlike $H_3B.PF_2PF_2$ which is

fluctional[156] even at 193 K. In the bis adduct, $^{1}J(P^{11}B)$ could not be accurately measured due to overlap with the second-order features of the ^{31}P spectrum.

Chapter 5

Difluorophosphino(tetrafluorophosphoranyl)amine

"All is flux, nothing stays still"

Heracleitus, 6th century B.C.

"Stop! Stop! Stop all the dancing,
Give me time to breathe"

"The Hollies", 1966.

Introduction

Although not previously unknown, mixed valency compounds of phosphorus are not the commonest of species[51,52,53,54], and of this select group, fully fluorinated phosphorus nuclei are only rarely met[52,55], compounds of the type P^{III}-X-P^{III} and P^{V}-X-P^{V} being commoner[34,35,48,49,50,51]. Synthesis of the known mixed valence species has been achieved by a number of routes including the following examples.

$2PF_2BrO$ + excess Hg $\xrightarrow{h\nu}$ $O(PF_2)(PF_2O)$ + Hg_2Br_2 ...5:1[54]

$NCH_3(SiMe_3)(PCl_2S)$ + PCl_3 → $NCH_3(PCl_2)(PCl_2S)$ + Me_3SiCl ...5:2[51]

$NCH_3(PCl_2)(PCl_2O)$ + excess NaF → $NCH_3(PF_2)(PF_2O)$ + NaCl ...5:3[55]

$2PF_2(NH_2)$ + PF_3Cl_2 → $PF_2(NPF_3)$ + PF_2Cl + NH_4Cl ...5:4[52]

Silicon-nitrogen bonds have long been known to be susceptible to attack by inorganic halides[43,46] and it is usually very straightforward

to predict the product of such a reaction (equation 5:5). Thus with

...5:5

for example $PF_2[NH(SiH_3)]$ or $PF_2[NH(SiMe_3)]$ a clear pathway to P^{III}-N-P^V compounds is available by reaction with a P^V halide. It was therefore decided to make $NH(PF_2)(PF_4)$, the parent compound for such bridged species. As hydrogen bonding is likely to lead to only one favourable orientation of the PF_2 group relative to the amino proton, as also happens[47] in $BF_2[NH(PF_2)]$, it can be predicted that only one N-H stretch will be found in the i.r. spectrum, unlike $PF_2[NH(MH_3)]$ (M=Si, Ge) and $PF_2[NH(SiMe_3)]$. It may be possible to make other nitrogen-bridged phosphorus fluorides via $PF_2[NH(SiH_3)]$ by utilising different P^V fluorides. (It transpires that independently of this work the compound $NMe(PF_2)(PF_4)$ has been synthesised by a similar route[55], and this is the only other example of a P^{III}-X-P^V species containing a five-coordinate P^V nucleus).

Results and Discussion

5:1 Preparation

The preparation of $NH(PF_2)(PF_4)$ was very facile indeed, Experimental Section 5:1, giving yields of ca. 90-95%. In fact it was not considered worthwhile to try and optimise the reaction conditions further.

$$PF_2[NH(SiH_3)] + PF_5 \rightarrow NH(PF_2)(PF_4) + SiH_3F \quad ...5:6$$

Also formed in trace amounts, via equation 5:7 was $PF_2(NPF_3)$, identified by i.r. spectroscopy[52]. Its greater volatility simplified its separation from $NH(PF_2)(PF_4)$. Reaction 5:7 also occurred when samples were irradiated with green laser light (488 nm) with almost the entire sample being converted to $PF_2(NPF_3)$. (See also the reactions with HX).

$$2NH(PF_2)(PF_4) \rightarrow PF_2(NPF_3) + "NH(PF_2)(PF_4).HF" \quad ...5:7$$

The only discordant note struck was the difficulty in removing the final traces of SiH_3F from the $NH(PF_2)(PF_4)$, even though their volatilities are vastly different. It is possible these two compounds form a hydrogen bonded adduct. This impurity made any attempt at vapour pressure or molecular weight studies futile.

The compound was normally prepared on a 1-1.5 mmole scale, as increasing this to 3 mmoles led to lower yields (ca. 70%), more $PF_2(NPF_3)$, and white solids. It is felt that similar results would be obtained using $PF_2[NH(SiMe_3)]$ instead of the SiH_3 compound, which may be preferable due to the latter's explosive nature.

The reaction between $PF_2(NH_2)$ and PF_5 was meant to simplify the synthesis of $NH(PF_2)(PF_4)$ by avoiding the preparation of $PF_2[NH(SiH_3)]$. But the only product from this liquid phase reaction was a white solid; traces of unreacted $PF_2(NH_2)$ were also recovered. It is interesting to speculate on this solid's identity.

There are two reasonably attractive possibilities. Firstly, $NH(PF_2)(PF_4)$ could have been formed, HF being the other product. Then the HF immediately reacts with the $NH(PF_2)(PF_4)$, giving the white solid, in a similar manner to the HBr, HCl, reactions, and as in reaction 5:7, the decomposition route suggested earlier. But any HF produced should also react with $PF_2(NH_2)$, giving PF_3 and NH_4F;

therefore some $NH(PF_2)(PF_4)$ and PF_3 should have been observed as their i.r. spectra are very intense.

Much more strongly favoured is adduct formation between PF_5 and $PF_2(NH_2)$. It has been reported[15,161] that PF_5 and NH_3 give a variety of solids of general formula $xPF_5.yNH_3$ ($5 \geq x$; $y \geq 1$), although later work on that system revealed that under certain conditions $PF_3(NH_2)_2$ could be formed instead[162]. As a mixture of adducts would be expected here, and decomposition to P-N polymer is possible, no attempt was made to analyse the solid. Although a gas phase reaction similar to Lustig's preparation[162] of $PF_3(NH_2)_2$ might be more successful, the ratio of reactants he used indicates a very complex reaction as an overall balanced equation could not be deduced. This implies that some adduct formation probably occurred, which would account for the low yields (41%) he reported.

5:2 General Properties

The vapour pressure of $NH(PF_2)(PF_4)$, which is a colourless, mobile, volatile liquid, could not be properly measured (see above), but it is greater than 10 cm Hg at 290 K, and the compound is very easily handled in a vacuum line. Practically involatile at 195 K, it was usually trapped out at that temperature or at 177 K at which temperature it is completely involatile.

Stable in the gas phase for at least 5 hours at 308 K, it has survived for an hour at temperatures as high as 374 K with only slight decomposition evident. Traces of white solids were noted sometimes after liquifying the compound, perhaps due to elimination of HF or reaction with water. When exposed to the air it produces white fumes, and when passed through a "wet" vacuum line, $O(PF_2)_2$, PF_3O, and a white solid, assumed to be NH_4F, are formed. It has a quite unpleasant odour, typical of all F_2PN compounds.

5:3 Vibrational Spectra

Details of the vibrational spectra of $NH(PF_2)(PF_4)$ are presented in Table 5:1. However detailed assignments of the modes have not been attempted as with nine atoms of comparable mass and at best one element of symmetry a complete vibrational analysis would be necessary. The compound has a very intense i.r. spectrum which aided identification of trace quantities of the amine but made good solid phase spectra very difficult to obtain.

The N-H stretch and deformation modes are particularly important. In the gas phase, there is only one band in each of the appropriate regions, indicating that there is probably only one gas phase conformer of $NH(PF_2)(PF_4)$, unlike $PF_2[NH(SiMe_3)]$ and $PF_2[NH(GeH_3)]$. In the solid phase at 77 K, νNH is shifted to lower frequency and splits into two, while δNH is shifted to higher frequency. These changes are typical of a highly hydrogen-bonded N-H group in the solid phase, presumably due to intermolecular contacts.

Bands characteristic of PF_2X[35,36,47] and $P^{V}FX$ groups[25,52,55,162,163] stretching and deformation modes occur in the usual regions e.g. $P^{III}F_2$ stretches at ∿800 cm^{-1}, $P^{V}F_{e_2}$ stretches at ∿1000 cm^{-1}, $P^{V}F_{a_2}$ stretches at ∿620 cm^{-1} and $P^{III}F_2$ deformation at 445 cm^{-1}. The individual assignment of most of the bands, especially below ∿500 cm^{-1}, however, is not practical.

Some of the bands shift upon ^{15}N substitution - 1030 to 1022, 911 to 903 and 784 to 775 cm^{-1} - which implies that these modes include substantial contributions from the two P-N stretches, which probably mix with the P-F stretches. It has been shown in previous chapters that P^{III}-N stretches occur at about 1000 cm^{-1} which agrees with the above suggestion.

Table 5:1

Vibrational Spectra (cm^{-1}) of $NH(PF_2)(PF_4)$

I.r. (gas)		I.r. (solid)	Raman (liquid)	Assignment
^{14}N	^{15}N			
3413 m	3513 m	3353 m	3410 s	νNH
		3303 m	3340 m	
2640 vw,br		2680 w		2x1328
1328 s		1376 m		δNH
		1342 s		
		1309 m		
1030 vs	1022 vs	1051 s	1005 w	νPF_{e2}
990 vs	992 vs	1002 s	993 vw	
911 s	903 sh	909 s	921 w,br	νPF_2
	889 vs			
886 vs		854 s	885 m,br	
833 vs	833 vs		836 s,br	νPF_2
818 sh	817 sh	819 sh,vs	810 m,br	
784 s	775 s	780 vs	789 s	δPN
		740 sh	755 m	
		686 m		
614 m	616 m	622 vw	635 m	νPF_{a2}
565 ms	569 ms	558 m	572 w	
541 m	544 m	539 m		$\delta PF_{e2}N$
515 m	516 m	516 m	518 w	
		482 w	494 w	deformations and torsions
		469 w	446 w	
445 m	446 m	442 w	440 w	
		427 w	433 w	
		418 w	414 w	
393 m	392 m	397 m	402 m	
358 w	- (a)		359 w	
350 w		350 w		
324 vw		323 w	333 w,br	
295 vw		301 w		
274 vw			276 s	
			226 m	
188 w				
162 w			155 mw,br	

s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder

Note:- a. Not investigated below 350 cm^{-1}

The Raman spectrum was obliterated by fluorescence when a green laser (488 nm) was used, and although better results were obtained using a red laser (647 nm), the quality was still rather low, and not much weight should be attached to this data.

5:4 N.m.r. Spectra

It is very common to find that the fluorine nuclei in five-coordinate P^V compounds are all magnetically equivalent - the ^{19}F n.m.r. of PF_5 for example shows only one doublet[164] and not, as might be expected, two doublets of multiplets due to inequivalent axial and equatorial fluorines. This is due to Berry pseudorotation[165] in which the fluorines exchange positions rapidly on the n.m.r. timescale. The phenomenon occurs in the vast majority of P^V compounds even at temperatures as low as 150 K[166,167,168,169]. But in some cases[170,171,172,173], due to certain structural peculiarities, this process can be considerably slowed down. The important factor is usually F--H interactions, and the spectra of $^{15}NH(PF_2)(PF_4)$ at 223 K are examples par excellence of the consequences of stopping Berry pseudorotation.

The parameters measured and the multiplicities of the various resonances are summarised in Tables 5:2, 5:3 and 5:4. All the spectra are first order. The following discussion of spectra ran in CD_2Cl_2/TMS applies equally well to $CDCl_3$ spectra, apart from temperature differences.

Description of Spectra

At 223 K in CD_2Cl_2/TMS the ^{19}F spectra contained four sets of resonances with relative intensities 2:2:1:1 which could be assigned,

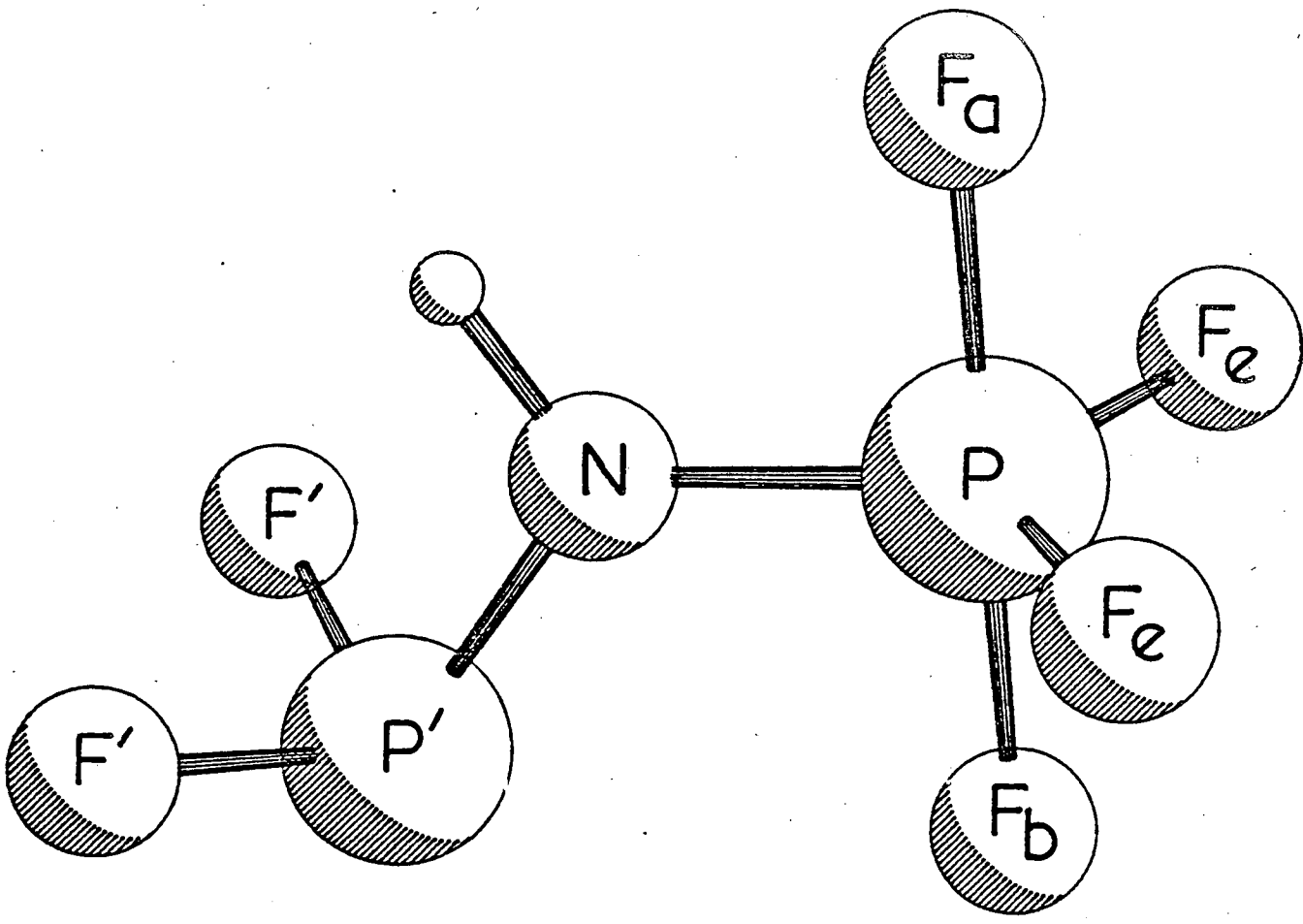


Figure 5:1 The proposed structure of $NH(PF_2)(PF_4)$ with the nuclei labelled as in Table 5:3.

Table 5:2

Couplings and Multiplicities in n.m.r. Spectra of $^{15}NH(P'F'_2)(PF_4)$

Nucleus		
^{31}P	3 x 2 x 2 x 2 x 2 x 3 x 2 F_e F_a F_b N P' F' H	5 x 2 x 2 x 3 x [2 a F N P' F' [H
$^{31}P'$	3 x 2 x 2 x 2 x 2 x 2 F' F_b N P F_a H	3 x 2 x 5 x 2 x [2 a F' N F P [H
$^{19}F_a$	2 x 3 x 2 x 2 x 2 P F_e P' N H	
$^{19}F_b$	2 x 2 x 3 x 2 x 3 x 2 P P' F_e H F' N	2 x 2 x 3 x ? b P P' F'
$^{19}F_e$	2 x 2 x 2 P F_a F_b	
$^{19}F'$	2 x 2 x 2 x 2 x 2 P' P F_b N H	2 x 2 x 5 x 2 x [2 P' P F N [H
^{1}H	2 x 2 x 3 x 2 x 2 x 2 N F_a F' F_b P P'	n.s.

note a. Assumed, decoupled spectra were studied

b. Fully resolved high temperature spectra were not obtained.

n.s. not studied

Table 5:3

N.m.r. Parameters of $^{15}NH(P'F'_2)(PF_4)$[a]

δ^1H	5.40 ppm[b]	$^2J(F_aF_b)$	<0.2 Hz
$\delta^{31}P$	-71.3 ppm	$^2J(F_aF_e)$	88.2
$\delta^{31}P'$	138.9 ppm	$^2J(F_bF_e)$	79.7
$\delta^{19}F_a$	-48.3 ppm	$^2J(F_a{}^{15}N)$	11.5
$\delta^{19}F_b$	-41.8 ppm	$^2J(F_b{}^{15}N)$	3.9±0.2
$\delta^{19}F_e$	-73.4 ppm	$^2J(F_e{}^{15}N)$	<0.2
$\delta^{19}F'$	-61.2 ppm	$^2J(F'{}^{15}N)$	3.4±0.2
$\delta^{15}N$	60 ppm[c]	$^3J(PF')$	16.1
$^1J(PF_a)$	801.7 Hz	$^3J(P'F_a)$	±14.7
$^1J(PF_b)$	766.5	$^3J(P'F_b)$	∓209.2
$^1J(PF_e)$	965.5	$^3J(P'F_e)$	<0.2
$^1J(P'F')$	1256.7	$^3J(F_aH)$	1.0
$^1J(P{}^{15}N)$	69.5	$^3J(F_bH)$	31.0
$^1J(P'{}^{15}N)$	84.0	$^3J(F_eH)$	<0.2
$^1J(^{15}NH)$	80.7[b]	$^3J(F'H)$	6.3
$^2J(PP')$	14.7	$^4J(F_aF')$	<0.2
$^2J(PH)$	1.0±0.05[b]	$^4J(F_bF')$	14.0
$^2J(P'H)$	1.0±0.05[b]	$^4J(F_eF')$	<0.2

a. In $CD_2Cl_2/SiMe_4$ at 223 K unless marked b.

b. In $CDCl_3$ at 187 K.

c. Error limits, +3, -4 ppm.

Table 5:4

Temperature Dependence of N.m.r. Parameters[a]

Parameter	220 K				333 K
	F_a	F_b	F_e	Weighted mean	Observed
$\delta^{19}F$ (ppm)	-48.3	-41.8	-73.4	-59.2	-59.4
$^1J_{PF}$ (Hz)	801.7	766.5	965.5	874.8	875
$^2J(F^{15}N)$ (Hz)	11.5	3.9	<0.2	7.7	n.r.
$^3J_{P'F}$ (Hz)	14.7	209.2	<0.2	56.0/48.6[b]	49
$^3J_{FH}$ (Hz)	1.0	31.0	<0.2	8.0	n.s.
$^4J_{FF'}$ (Hz)	<0.2	14.0	<0.2	3.5	4.9

Other Parameters[b]	187 K	374 K
δP (ppm)	-71.2	-68.7
$\delta P'$ (ppm)	+136.3	+138.7
δF (ppm)	-61.2	-60.3
$^1J_{PF'}$ (Hz)	1258.9	1262
$^1J(P'^{15}N)$ (Hz)	84.0	83.2
$^1J(P^{15}N)$ (Hz)	69.5	67.7
$^2J_{PP'}$ (Hz)	14.7	12.3
$^2J(F'^{15}N)$ (Hz)	4.0	4.7
$^3J_{PF'}$ (Hz)	15.8	15.7

Notes: a. In $CD_2Cl_2/SiMe_4$.

b. In $CDCl_3$, remaining parameters not studied.

n.r. Not resolved.

n.s. Not studied.

on the basis of multiplicities (Table 5:2) and magnitude of couplings (Table 5:3), to the fluorine atoms F′, F_e, F_a and F_b (Figure 5:1). The presence of three chemically distinct types of fluorine in the $-PF_4$ group implies that not only is Berry pseudorotation exchange between the equatorial and axial sites slow on the n.m.r. time scale but also that there is restricted rotation about the P-N bond, resulting in the two axial fluorines becoming chemically non-equivalent. This is probably due to interactions between F_a and the proton, and also between F′ and the proton. This interpretation also agrees with the general rule that the most electronegative groups will occupy the axial positions.

Similarly, at 223 K the ^{31}P spectra showed two sets of resonances, the higher frequency signals being assigned to P′ and the lower frequency ones to the P^V nucleus. These resonances coupled with several of the other spinning nuclei, the P^V nucleus coupling to all of the seven other groups of nuclei, giving 288 lines in all - Figures 5:2 and 5:3. Six groups of nuclei coupled to the single proton.

When the CD_2Cl_2/TMS solution was warmed to 228 K the ^{19}F spectrum changed drastically and only the F′ resonances were well defined, with gently rising very broad humps discernable where the other resonances had been. From 233 K to 273 K even these humps were undetectable, only coalescing at 293 K, but the spectra had still not reached the high-temperature limit at 353 K, the highest temperature considered safe for sealed tubes containing these solvents. However the F′ resonances showed that from 228 K upwards the four phosphoranyl fluorines were equivalent with respect to these fluorines.

Repeating the variable temperature study using $CDCl_3$ as solvent,

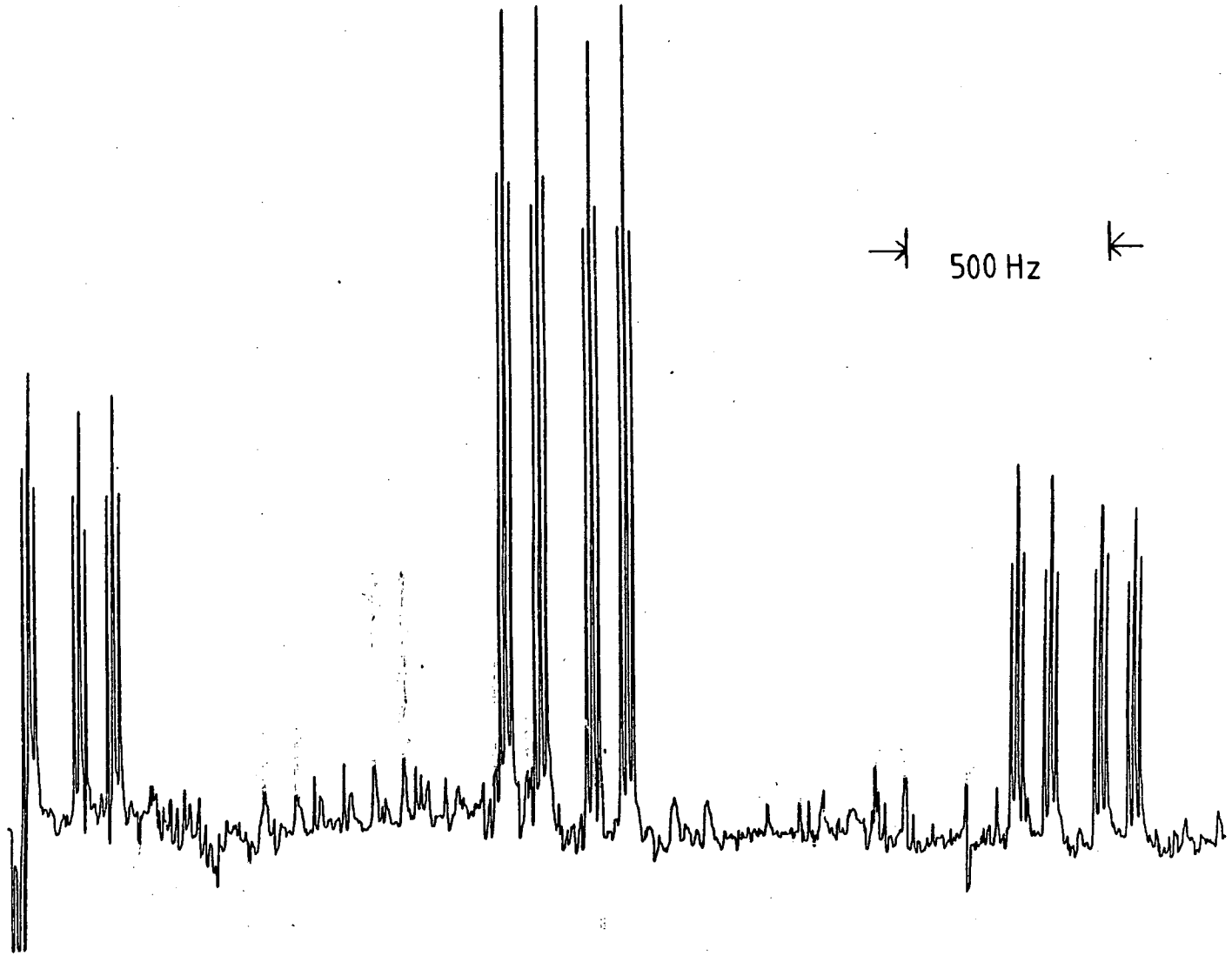


Figure 5:2 A. ^{31}P n.m.r., ^{1}H decoupled, of P^{III} in $^{15}NH(PF_2)(PF_4)$, at 223K.

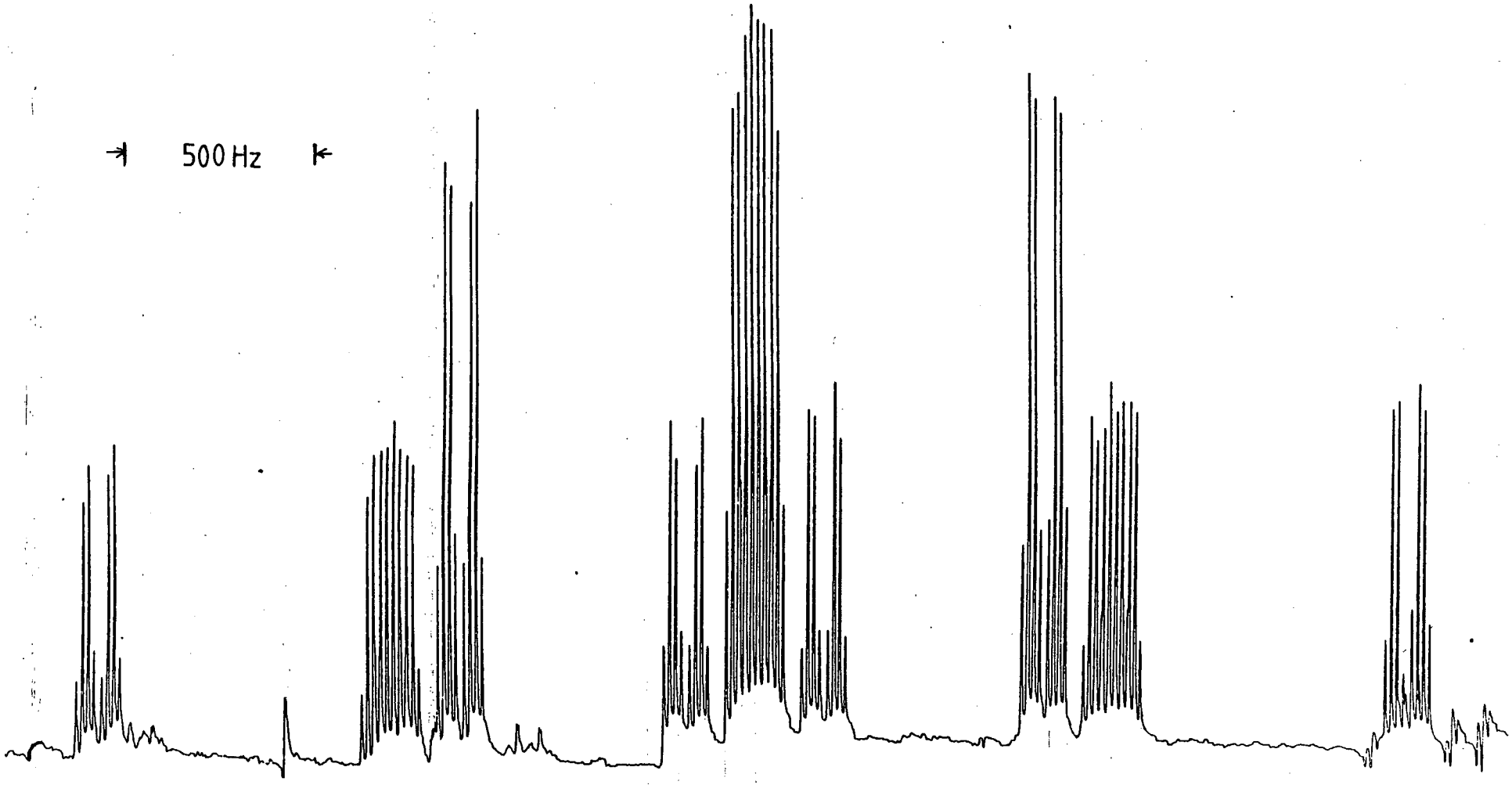


Figure 5:2 B. ^{31}P n.m.r., ^{1}H decoupled, of P^{V} in $^{15}NH(PF_2)(PF_4)$, at 223K.

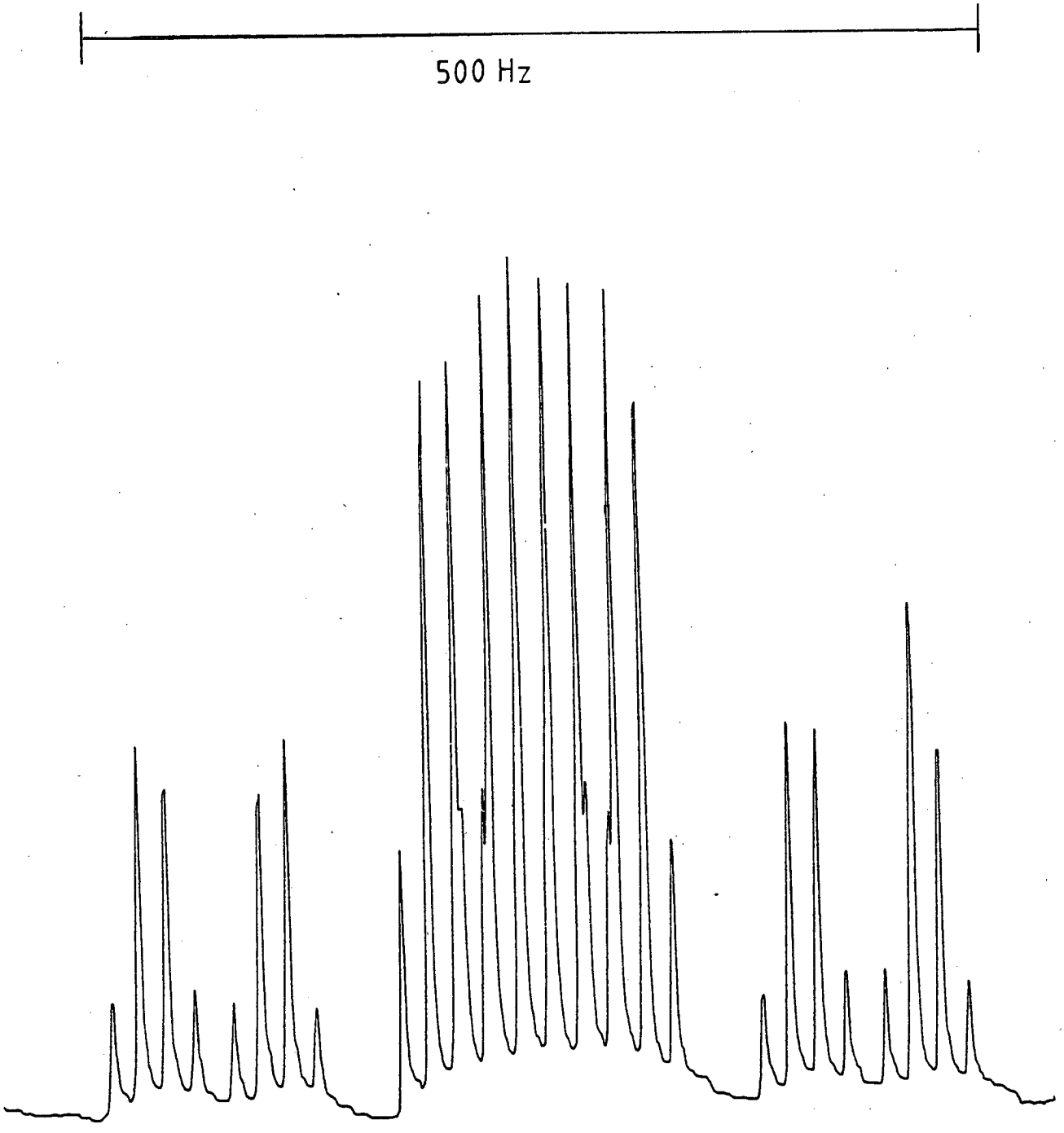


Figure 5:2 C. The central multiplet of Figure 5:2B.

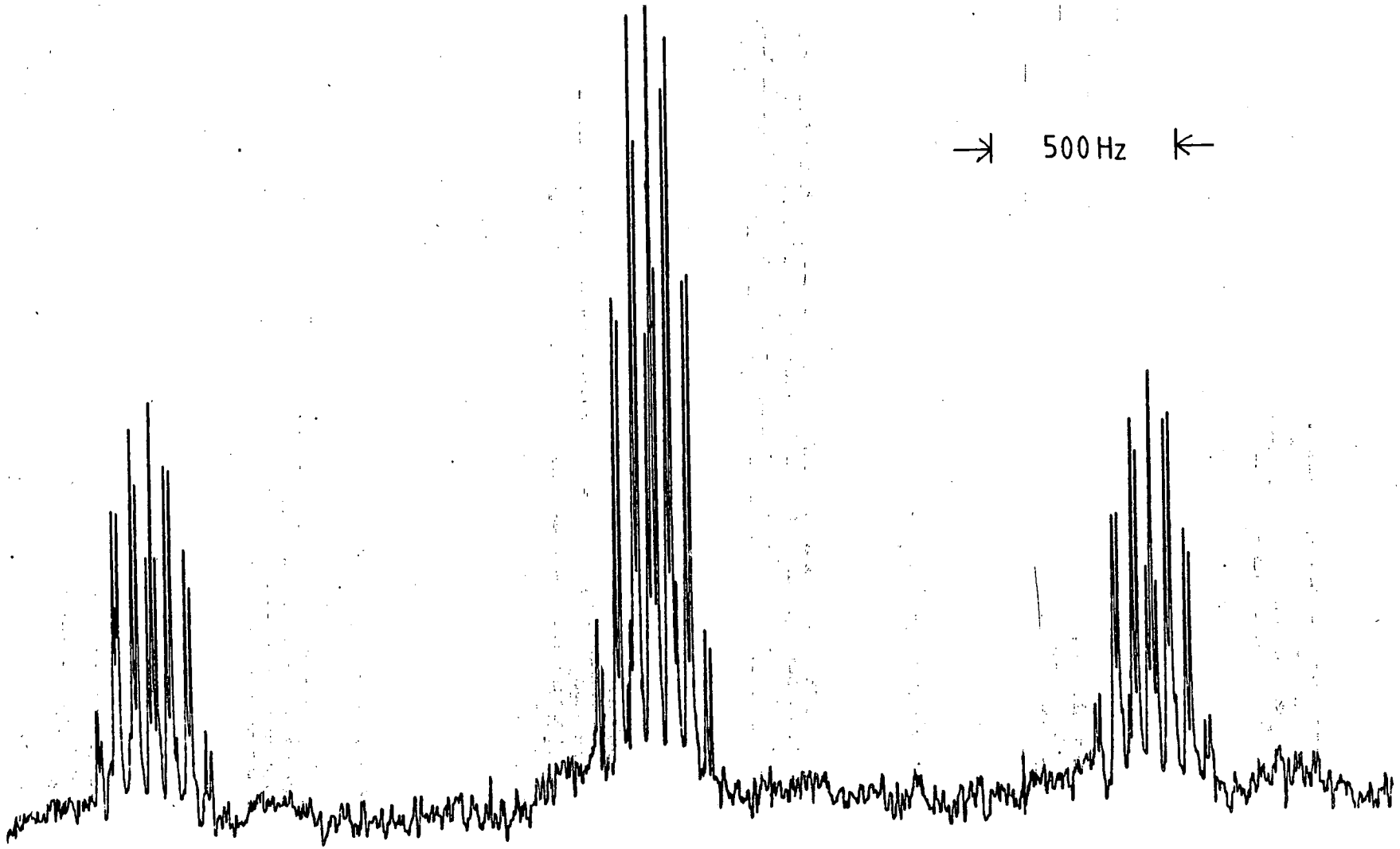


Figure 5:3 A. ^{31}P n.m.r., ^{1}H decoupled, of P^{III} in $^{15}NH(PF_2)(PF_4)$, at 323K.

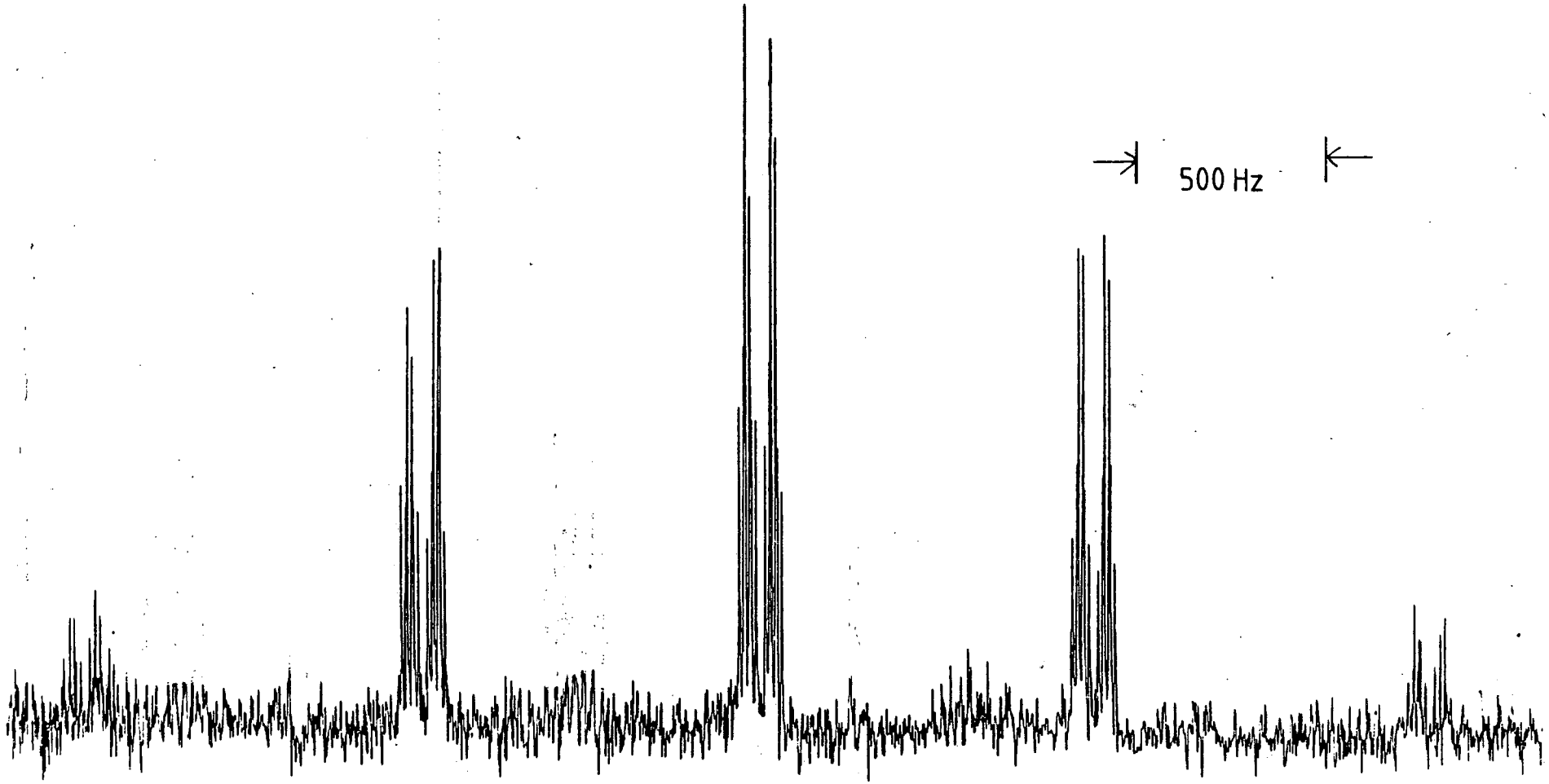


Figure 5:3 B. ^{31}P n.m.r., ^{1}H decoupled, of P^{V} in $^{15}NH(PF_2)(PF_4)$, at 323K.

it was necessary to go to lower temperatures than were required in the earlier experiments in order to achieve similar "frozen out" spectra. This implies that external factors can influence the rate of intramolecular pseudorotation, probably via intermolecular hydrogen bonding between the solvent and the P^V fluorines. Such interactions will be more numerous in CD_2Cl_2 than $CDCl_3$, hence the fluorines will be held more rigidly and pseudorotation will be slower at any given temperature.

The $-PF_2$ group fluorine resonances were now sharp at 187 K but poorly resolved at 215 K, and by 231 K had reached the high temperature limit. The P and P′ resonances were still well resolved at 218 K but at 298 K were broad and only reached their high-temperature form at ca. 320 K. At 187 K, the three different $-PF_4$ group fluorine resonances were sharply resolved, indicating that fluorine exchange had been arrested, but signs of broadening were obvious by 215 K. At 231 K broad humps were all that remained of these resonances, though still in their original positions. These degenerated into gentle rises barely discernable from the base line (forming a single band some 5 KHz wide between 240 and 290 K) until at 299 K a pair of broad resonances in the mean position could be observed - Figures 5:4, 5:5 and 5:6. Although fine structure on these peaks began to appear at 329 K and the resonances were approaching the high-temperature limit at 374 K, the highest temperature deemed to be safe, the smallest couplings could still not be resolved.

As the three sets of $-PF_4$ group fluorine resonances collapse into a single set, retaining couplings to the other nuclei, this indicates an intramolecular rearrangement process is occurring. There is no evidence to indicate that the axial fluorines exchange

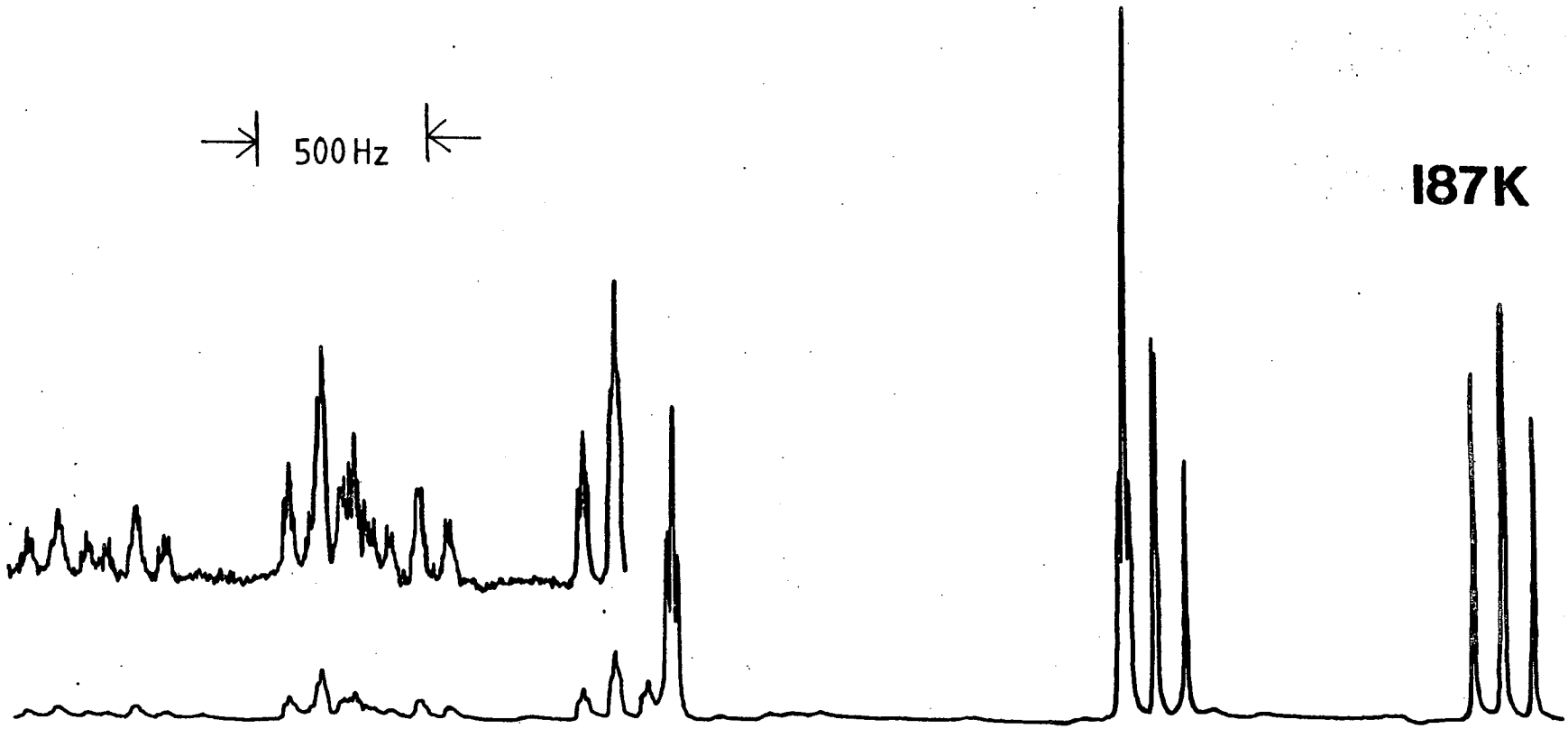


Figure 5:4 ^{19}F n.m.r., ^{1}H decoupled, of $^{15}NH(PF_2)(PF_4)$ at 187K.

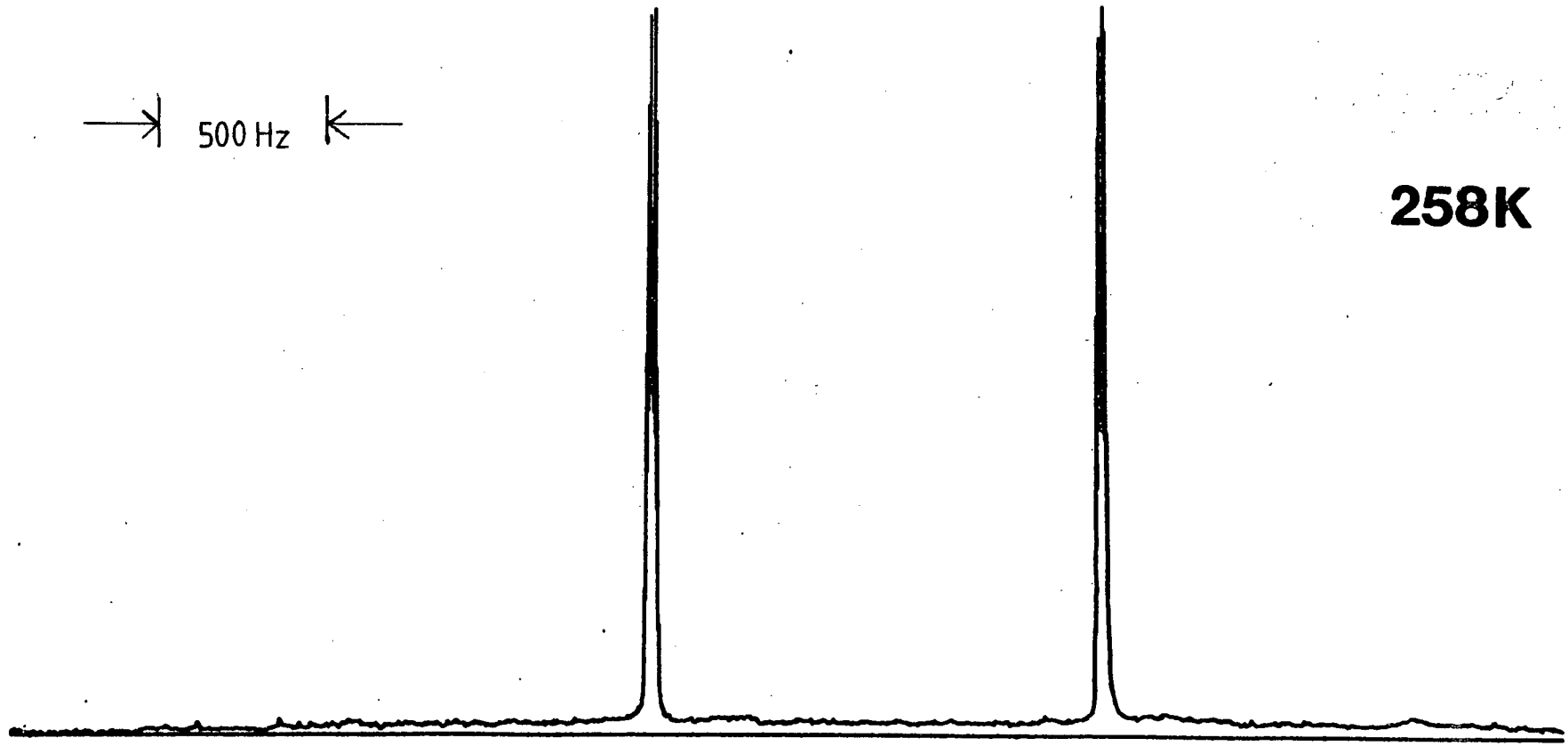


Figure 5:5 ^{19}F n.m.r., ^{1}H decoupled, of $^{15}NH(PF_2)(PF_4)$ at 258K.

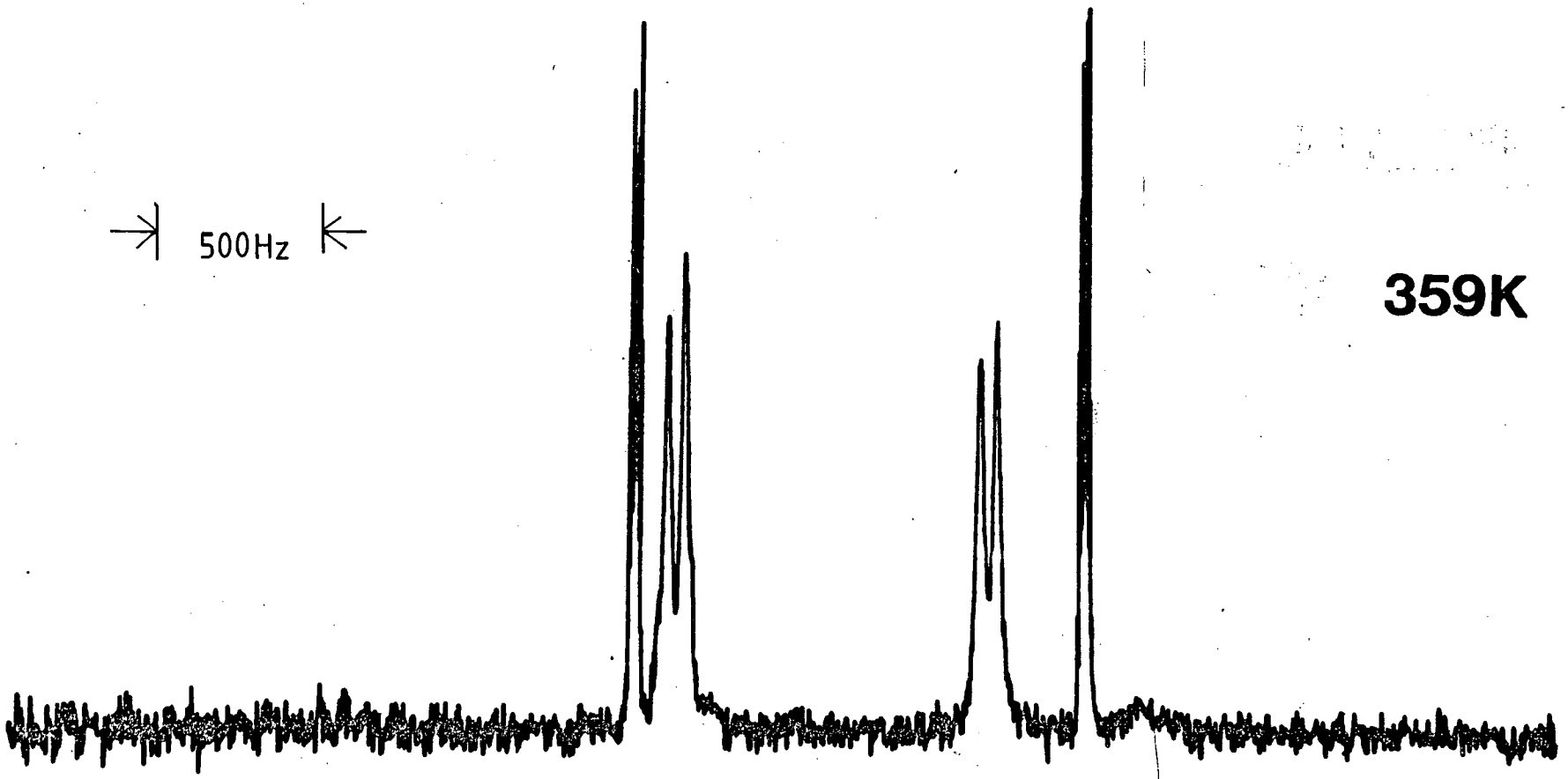


Figure 5:6 ^{19}F n.m.r., ^{1}H decoupled, of $^{15}NH(PF_2)(PF_4)$ at 359K.

with each other prior to the onset of axial-equatorial exchange, which implies that rotation about the P-N bond cannot commence before pseudorotation.

Chemical Shifts

The relative intensitives of the ^{19}F resonances at low temperatures made assignments easy, as did the different $^{1}J_{PF}$'s. The F′ nuclei are typical[31,35] for a $PF_2N<$ compound. The equatorial fluorines are responsible for the lowest frequency lines, and the two highest frequency multiplets are due to the two different axial fluorines. Similar differences in δF for axial and equatorial fluorines have been noted before[25,166,167,169,171,172,173] and are useful in differentiating between the two positions.

The question as to which axial fluorine goes with which set of multiplets is answered in the Coupling Constants section. The weighted average of the three different $-PF_4$ fluorines is in very close agreement with $\delta(F_{aver})$ observed in the high temperature spectra (Table 5:4). The two sets of ^{31}P resonances are in the characteristic regions[31,55,62,170] for P^{III} and P^{V} species like these. The large difference in δP between P and P′ is one of the commonest ways[62] of establishing phosphorus oxidation states from n.m.r. spectra.

The variation of δH across the series $PF_2(NH_2)$[83] (δ = 3.23 p.p.m.) $NH(PF_2)_2$[35] (δ = 4.38 p.p.m.) and $NH(PF_2)(PF_4)$ (δ = 5.40 p.p.m.) shows the expected high frequency shift with increasing electronegativity of the substituents. Although only measured approximately, during an $\{^{15}N\}$ experiment on the proton spectra, $\delta(^{15}N)$ shows the expected high frequency shift compared to $PF_2(^{15}NH_2)$[83] (δ = +21 p.p.m.) due to the more electronegative substituents on the nitrogen. Small changes

in most of these parameters occurred when $CDCl_3$ was used as solvent.

Coupling Constants

The focal point for attention in these spectra must be the coupling constants, some of which are extremely unusual, and only 6 of the 28 couplings were too small to be resolved.

The electron withdrawing PF_4 group on the nitrogen results in a slightly larger than normal $^1J(P'F')$ for a PF_2N compound[31,35]. As usual[166,167,170], the equivalent couplings for the P^V fluorines are much smaller, due to the different orbitals used for bonding and their different s character, and the $^1J(PF_{axial})$'s are smaller than $^1J(PF_e)$. In the high temperature spectra the observed $^1J(PF_{aver})$ is in excellent agreement with the weighted average of the three different couplings.

The differing s character of the two P-N bonds is also crucial in determining $^1J(P^{15}N)$, as was discussed in Chapter 3, and the two couplings here are therefore probably of opposite sign, with $^1J(P'^{15}N)$ = +84.0 Hz and $^1J(P^{15}N)$ = -69.5 Hz. In a similar vein, Binsch[174] has suggested a relationship between $^1J(^{15}NH)$ and s character, and hence the geometry about the nitrogen. The coupling here predicts 28.6% s character in the N-H bond and as Binsch's equation ($\%s_{N-H} = 0.43\,J(^{15}NH) - 6$) tends to underestimate s character for a few known planar nitrogens in P-F systems[36,170], this would imply that the nitrogen here is probably planar.

The value of $^2J_{PP}$ is dependent upon the phosphorus nuclei's oxidation state and the value here seems fairly typical[69] for a $^2J(P^VNP^{III})$. This coupling is much smaller than that of $N(PF_2)_2(SiH_3)$, but large values of $^2J_{PP}$ are associated with lone pair - lone pair interactions and such interactions are impossible between P^{III} and P^V.

Three quite different values of $^2J(FP^V{}^{15}N)$ are observed. While $^2J(F_e{}^{15}N)$ is too small to be resolved (which also appears[175] to be the case in $PF_4(^{15}NH_2)$), $^2J(F_a{}^{15}N)$ = 11.5 Hz and $^2J(F_b{}^{15}N)$ = 3.9 Hz. Although $^2J(F_a{}^{15}N)$ is comparable with the few other such couplings reported[170,175], $^2J(F_b{}^{15}N)$ is unusually small. From the dearth of data available, it would seem that larger $^2J(F_a{}^{15}N)$'s are encountered when F--H(N) interactions are possible i.e. when two possible coupling pathways exist, and this suggests that F_a is cis to the proton. While similar reasoning might apply to $^2J(F^{15}N)$ in the $PF_2(NRR^1)$ series (R,R^1 = H, SiH_3, GeH_3), this makes $^2J(F'{}^{15}N)$ here seem a bit small. Unfortunately, $^2J(F_{aver}{}^{15}N)$ was not resolved in the high-temperature spectra.

Similarly, $^3J(F_eH)$ was not resolved, $^3J(F_aH)$ = 1 Hz, but $^3J(F_bH)$ = 30 Hz. It is tempting to say F_b is adjacent to the proton, and F--H interactions cause the large coupling. But this idea is rejected in preference to a new hypothesis. Karplus's work[65] on variations in vicinal HH couplings with dihedral angle is well known and such systems have been well investigated[66]. The variation of $^3J_{FCCH}$ in fluoroethanes has also been studied[67,68] and follows an identical relationship, showing a maximum for a dihedral angle of 180°, with a smaller maximum at 0°, and minima at 90° and 270°. On the basis of the above $^3J_{FH}$'s it is suggested that there is a similar relationship between $^3J_{FPNH}$ and dihedral angle. This implies that F_b is trans to the proton. It must be admitted that other workers in this sort of situation have preferred to assign the axial fluorine with the largest coupling as cis to the proton[25,117,170,172,175] But applying the new hypothesis to the small $^3J(F'P'NH)$ results in the reasonable prediction that these fluorines are close to cis to the proton i.e. as in Figure 5:1; and in $PF_2[NH(GeH_3)]$, where the opposite

orientation of the PF_2 group was suggested due to F--H(Ge) interactions, $^3J_{FH}$ is correctly predicted as large. However, as rotation about the P-N bond would average $^3J_{FH}$, care must be taken to make deductions as to conformation only from low temperature spectra with "frozen in" structures, or rigid molecules. Unfortunately $^3J(F_{aver}H)$ was not studied in the high temperature spectra.

The deciding factor as to which axial fluorine is which has got to be the unusual values of $^3J(P'F)$, which was not resolved for F_e, 14.7 Hz for F_a and 209.2 Hz for F_b. There seems no logical explanation for such differences until the molecular geometry is considered. As regards the equatorial fluorines, in molecules where the P^V fluorines are directed away from the P^{III} nucleus, $^3J_{P'F}$ is always small. In $PF_2(NPF_3)$[52], which probably has a wide PNP angle, if not linear, $^3J(P'F)=0$, and in $NMe(PF_2)(PF_2O)$[55], which probably has all four fluorines interacting with the methyl protons, $^3J(P'F) = 1$ Hz.

As for the axial fluorines, the Karplus cis-trans argument quickly springs to mind but it is very unusual to find any 3-bond coupling as large as 200 Hz. For $P^{III}NP^{III}$ linkages, $^3J(P'F)$ is usually 30-45 Hz[35,97]. Therefore while $^3J(P'F_a) = 14.7$ Hz seems reasonable, albeit on the small side, perhaps a different mechanism is responsible for the much larger $^3J(P'F_b)$. Although F--H interactions can be suggested, this would still be a 3-bond route and seems unlikely to contribute much more to $^3J(P'F)$ than in say $NH(PF_2)_2$[35] where $^3J(P'F) = 21$ Hz.

Sketching the likeliest structure reveals a much more fascinating possibility (Figure 5:7). Using reasonable bond lengths and angles, it transpires that the P^{III} nucleus is approximately 2.2 Å from the

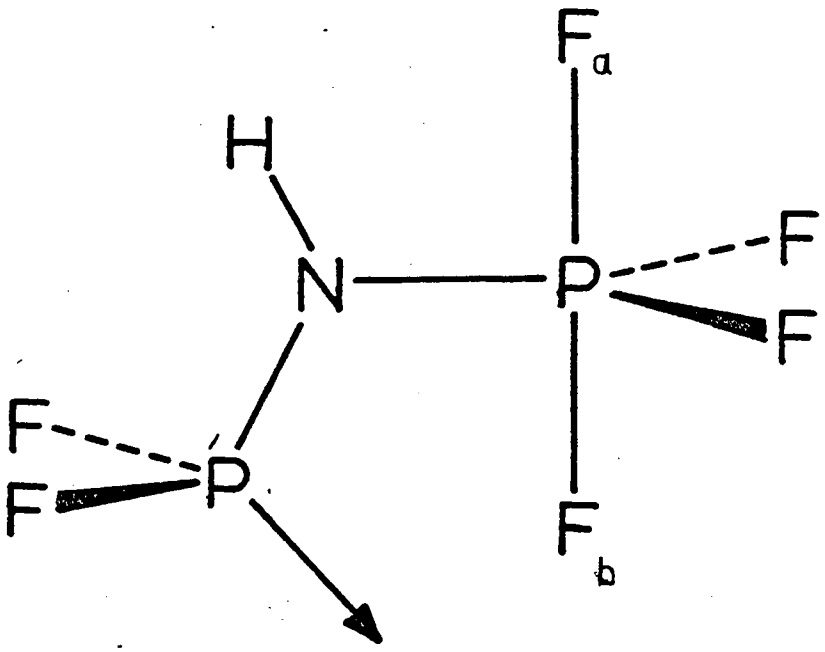


Figure 5:7 The axis of the P^{III} lone pair pointing at F_b.
r $P^{V}F_{ax}$ = 1.6 Å r $P^{V}N$ = 1.6 Å; r $P^{III}N$ = 1.6 Å; r NH = 1.0 Å
angles at N = 120°. H -- F_a ~ 2.2 Å, P' -- F_b ~ 2.2 Å.

closest axial fluorine - well within the sum of their van der Waal's radii, 3.15 Å. Although some distortion of the idealised geometry of Figure 5:7 probably does occur, it is suggested that a strong through-space interaction between these two nuclei via the P lone pair results in the large $^3J(P'F_b)$, and the axial F's are assigned as in Figure 5:1. Once again, as in Chapters 3 and 4, the lone pair directly influences a coupling constant. This also clarifies why fluorines directed away from a P^{III} nucleus have a very small $^3J(P'F)$, as they cannot interact with the lone pair. It is also of interest that in several of the examples quoted in Table 3:3, the two couplings are of different sign (with K being positive for the larger coupling whether it was over two or three bonds, implying a through-space interaction). In the variable temperature study, $^3J(P'F_{aver})$ = 49 Hz. But the weighted mean value is 56.0 Hz. This implies that either one or more of these couplings is very temperature dependent or that $^3J(P'F_a)$ and $^3J(P'F_b)$ are of opposite sign. The latter suggestion leads to $^3J(P'F_{aver})$ = 48.6 Hz, in excellent agreement with the experimental result, thus supporting the view that two different coupling mechanisms are involved. There is also evidence from the mass spectrum for some interaction between the P^{III} and a fluorine on the P^V - a rearrangement involving a fluorine transfer from P^V to P^{III} apparently occurs. Returning to δF_{axial}, δF_b is to higher frequency than δF_a and this agrees with the observation[176] that protons and carbons trans to a lone pair are at lower frequency than those in the cis position. In contrast to these odd couplings, $^3J(PF')$ is fairly typical cf. $NMe(P'F'_2)(PF_4)$, $^3J(PF')$ = 3.7 Hz[55]; $P'F'_2(NPF_3)$, $^3J(PF')$ = 24.1 Hz[52].

Another manifestation of the lone pair cis-trans effect causes $^2J(P'H)$ to be an order of magnitude smaller than usual[25,36,87]. The proton is almost certainly trans to the lone pair due to F--H interactions, in contrast to $PF_2[NH(GeH_3)]$ (Chapter 3) where the proton is cis and $^2J_{PH}$ is larger than usual. Why $^2J_{PH}$ is also small is not clear though.

As regards the various F-F couplings, $^2J(F_eF_a)$ and $^2J(F_eF_b)$ are both fairly typical[25,162,169,172,173,175] (80-90 Hz) but $^2J(F_aF_b)$ was not resolved. However Schmutzler[173] has reported some very small $^2J(F_aF_b)$'s in PF_4SR compounds as did Sharp[25] for $PF_4[NH(CH_3)]$, so $^2J(F_aF_b)$ here is not unusual. Finally $^4J(F_eF')$ and $^4J(F_aF')$ are too small to resolve due, of course, to the number of intervening bonds, while $^4J(F_bF') = 14.7$ Hz. This can be rationalised as the proposed interaction between F_b and the P lone pair results in a much shorter coupling pathway for F_b and F'. Considering the alternative assignment of F_a and F_b, the suggestion that this coupling is due to two interacting F--H interactions seems less feasible, especially since in $NH(PF_2)_2$ with the same possible route available, $^4J(FF')$ is only 5.4 Hz[35]. In the high temperature spectra, $^4J(F'F_{aver}) = 4.9$ Hz, while the weighted average is 3.6 Hz, suggesting some temperature dependence of these couplings.

5:5 Mass Spectrum

It was possible to recognise a large number of species which were present in the mass spectrum of $NH(PF_2)(PF_4)$, listed in Table 5:5. It can clearly be seen that, at low ionisation potentials, the dominant species is $[PF_3(NH)]^+$ (m/e = 103), with $[PF_2(NPF_3)]^+$ (m/e = 171) the next most prominant, as opposed to $[PF_2]^+$ at 70 eV. This indicates that the main dissociation route after ionisation is equation 5:8,

Table 5:5

Mass Spectrum of $NH(PF_2)(PF_4)$

m/e	Relative Abundance at 70 eV	Relative Abundance at 16 eV	Ion
191	2	3	$[NH(PF_2)(PF_4)]^+$
190	0.2		$[N(PF_2)(PF_4)]^+$
173	0.7		^{15}N
172	12.5	0.7	$[NH(PF_2)(PF_3)]^+$
171	54	72	$[N(PF_2)(PF_3)]^+$
153	9	17	$[NH(PF_2)_2]^+$
152	43	9	$[N(PF_2)_2]^+$
145	<0.05		$[PF_6]^+$
134	1.5		$[NH(PF_2)(PF)]^+$
133	3.5	5	$[N(PF_2)(PF)]^+$
123	~0.05		$[NH_2(PF_4)]^+$
122	~0.05		$[NH(PF_4)]^+$
121	<0.05		$[N(PF_4)]^+$
115	~0.05		$[NH(PF_2)(P)]^+$
114	0.4		$[N(PF_2)(P)]^+$
107	79	8	$[PF_4]^+$
104	54	14	$[NH_2(PF_3)]^+$, $[O(PF_3)]^+$, ^{15}N
103	85	100	$[NH(PF_3)]^+$
102	1.2		$[N(PF_3)]^+$
95	0.3		$[N(PF)(P)]^+$
88	18	11	$[PF_3]^+$
86	3	3.5	^{15}N
85.5	0.05		$[NH(PF_2)(PF_4)]^{++}$
85	48	4	$[PF_2(NH_2)]^+$, $[O(PF_3)]^+$
84	3.5		$[PF_2(NH)]^+$
83	0.8		$[PF_2N]^+$

cont/d...

Table 5:5 cont/d...

m/e	Relative Abundance at 70 eV	at 16 eV	Ion
77	1.5	2.5	$[NH(P)_2]^+$
76.5	0.1		$[NH(PF_2)_2]^{++}$
76	1	1	$[NP_2]^+$
70	0.2		$[PF_2H]^+$
69	100	5	$[PF_2]^+$
66.5	5		$[N(PF_2)(PF)]^{++}$
66	2.5	1	$[PF(NH_2)]^+$, $[OPF]^+$
65	10	11	$[PF(NH)]^+$
64	1.5		$[PF(N)]^+$
52	0.5		$[PFH_2]^+$
51	0.7	0.4	$[PFH]^+$
50	7	1	$[PF]^+$
47.5	~0.05		$[N(PF)(P)]^{++}$
47	4	0.4	$[PNH_2]^+$, $[PO]^+$, ^{15}N
46	14	0.5	$[PNH]^+$
45	1.5		$[PN]^+$
44	1.5		$[PF_3]^{++}$
42.5	0.3		$[PF_2(NH_2)]^{++}$
38	0.5		$[F_2]^+$
34.5	0.3		$[PF_2]^{++}$
33	0.5		$[FN]^+$
31	1.5		$[P]^+$
23.5	0.1		$[P(NH_2)]^{++}$
20	4		$[HF]^+$
19	0.2		$[F]^+$

cont/d...

Table 5:5 cont/d...

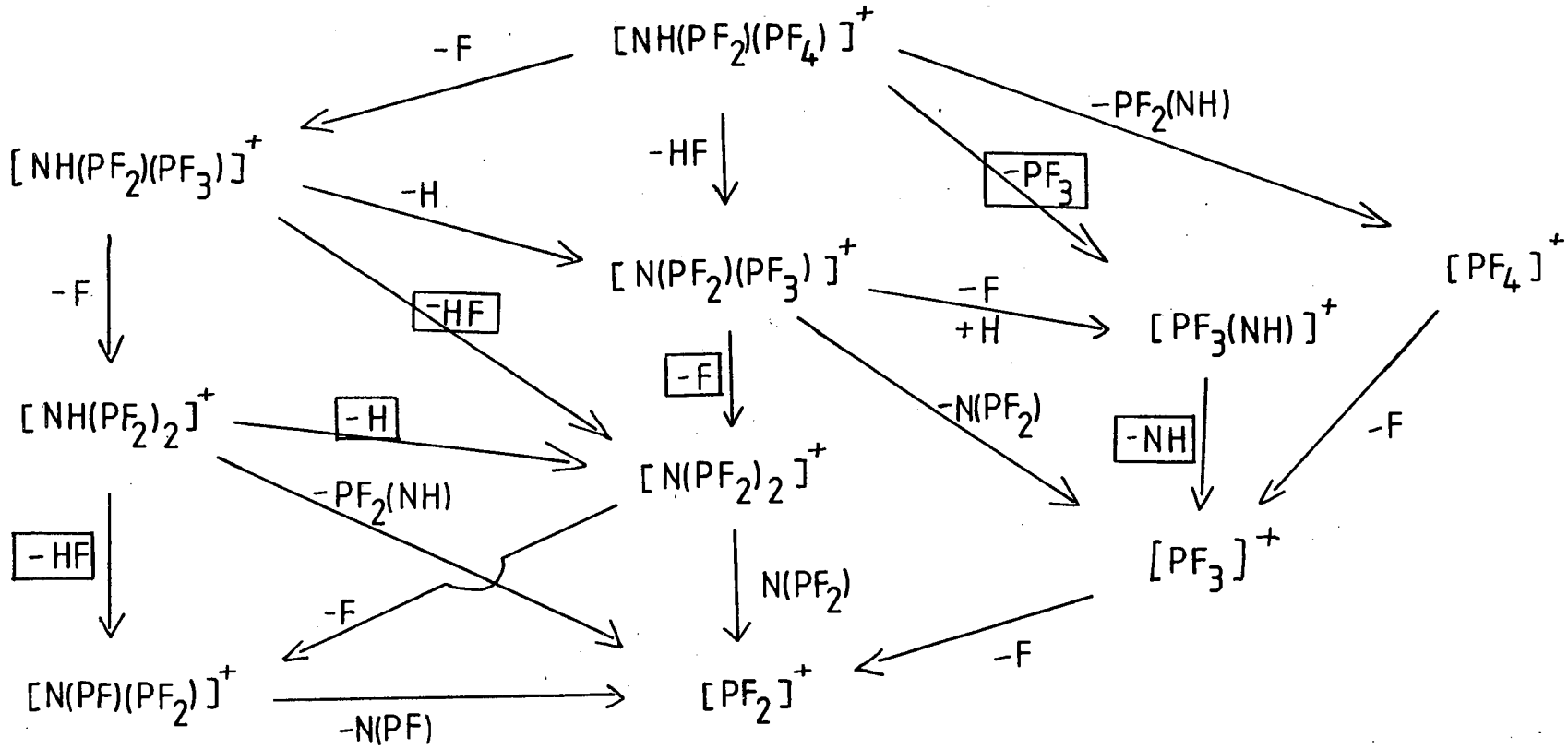
Metastables

55.5 (w)	$[NH(PF_2)(PF_4)]^+$	→	$[NH(PF_3)]^+$	+	PF_3
75.2 (w)	$[NH(PF_3)]^+$	→	$[PF_3]^+$	+	NH
115.6 (w)	$[NH(PF_2)_2]^+$	→	$[N(PF_2)(PF)]^+$	+	HF
134.3 (w)	$[NH(PF_2)(PF_3)]^+$	→	$[N(PF_2)_2]^+$	+	HF
135.1 (w)	$[N(PF_2)(PF_3)]^+$	→	$[N(PF_2)_2]^+$	+	F
151.0 (w)	$[NH(PF_2)_2]^+$	→	$[N(PF_2)_2]^+$	+	H

Exact mass of $NH(PF_2)(PF_4)$

Calculated	190.948635
Theoretical	190.948839
Error	<2 ppm.

Table 5:5A Breakdown routes of the major ions.



Notes a Table is incomplete for reasons of clarity.

b ☐ = a metastable peak corresponding to the loss of this species was observed.

c $[PF_2(NH_2)]^+$ and $[NH_2(PF_3)]^+$ have been omitted as the NH_2's may possibly be an O atom.

Table 5:6

Mass Spectrum[52] of $PF_2(NPF_3)$

m/e	Relative Abundance	Ion
171	38.7	$[PF_2(NPF_3)]^+$
152	25.8	$[N(PF_2)_2]^+$
102	54.8	$[NPF_3]^+$
88	trace	$[PF_3]^+$
83	12.9	$[PF_2N]^+$
69	100	$[PF_2]^+$
64	3.2	$[PFN]^+$
50	21.0	$[PF]^+$
45	8.1	$[PN]^+$
31	3.2	$[P]^+$

$$[NH(PF_2)(PF_4)]^+ \rightarrow [PF_3(NH)]^+ + PF_3 \quad \ldots 5:8$$

and this rearrangement corresponds to the metastable peak at m/e = 55.5. A possible mechanism for this rearrangement could involve the transfer of the axial fluorine of the P^V nearest to the P^{III} (Figure 5:8), which supports the previously postulated interaction of this fluorine with the P^{III}'s lone pair. The breakdown of $[PF_3(NH)]^+$, equation 5:9,

$$[PF_3(NH)]^+ \rightarrow [PF_3]^+ + NH \quad \ldots 5:9$$

is responsible for the metastable peak at m/e = 75.2, and also the strong $[PF_3]^+$ peak, which was only barely noticeable in the mass spectrum of $PF_2(NPF_3)$ (Table 5:6)[52]. The strong peak assigned to $[PF_2(NPF_3)]^+$ corresponds to the loss of HF by the parent compound, which is also the observed decomposition route at ambient temperature.

The other major breakdown pathways are loss of $PF_2(NH)$, leaving $[PF_4]^+$, m/e = 107, while the resultant $PF_2(NH)$ may be protonated to give $[PF_2(NH_2)]^+$. The obvious fragmentation routes - loss of F, H, and HF occur several times, and several metastable peaks are also present.

$$[NH(PF_2)_2]^+ \rightarrow [N(PF)(PF_2)]^+ + HF \quad (m/e = 115.6) \quad \ldots 5:10$$

$$[NH(PF_2)_2]^+ \rightarrow [N(PF_2)_2]^+ + H \quad (m/e = 151.0) \quad \ldots 5:11$$

$$[PF_2(NPF_3)]^+ \rightarrow [N(PF_2)_2]^+ + F \quad (m/e = 135.1) \quad \ldots 5:12$$

$$[NH(PF_2)(PF_3)]^+ \rightarrow [N(PF_2)_2]^+ + HF \quad (m/e = 134.3) \quad \ldots 5:13$$

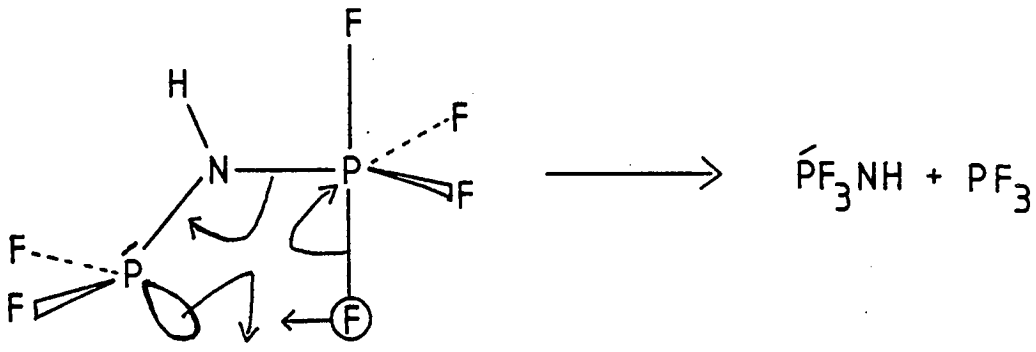


Figure 5:8 Probable mechanism for transferring an F to the P^{III} atom, giving the metastable peak at m/e = 55.5 in the mass spectrum.

Table 5:7

Photoelectron Spectra

Ionisation Potential (eV)		
$NH(PF_2)(PF_4)$	$PF_2(NPF_3)$	Assignments
11.65	11.2	$N2p_z$
12.7	12.6	$P2p_z$, ?P-Nπ
15.55	16.25	P-Nσ, N-Hσ
16.2))	17.6	$F2p_\pi$
17.35)		
17.8	18.0))	P-Fσ
18.6	18.6)	

As the first two metastables were also noted in the spectrum of $NH(PF_2)_2$[35], their presence here supports the structure $[NH(PF_2)_2]^+$ as opposed to $[NH(P)(PF_4)]^+$, implying that the fluorines are more easily lost by the P^V than the P^{III}.

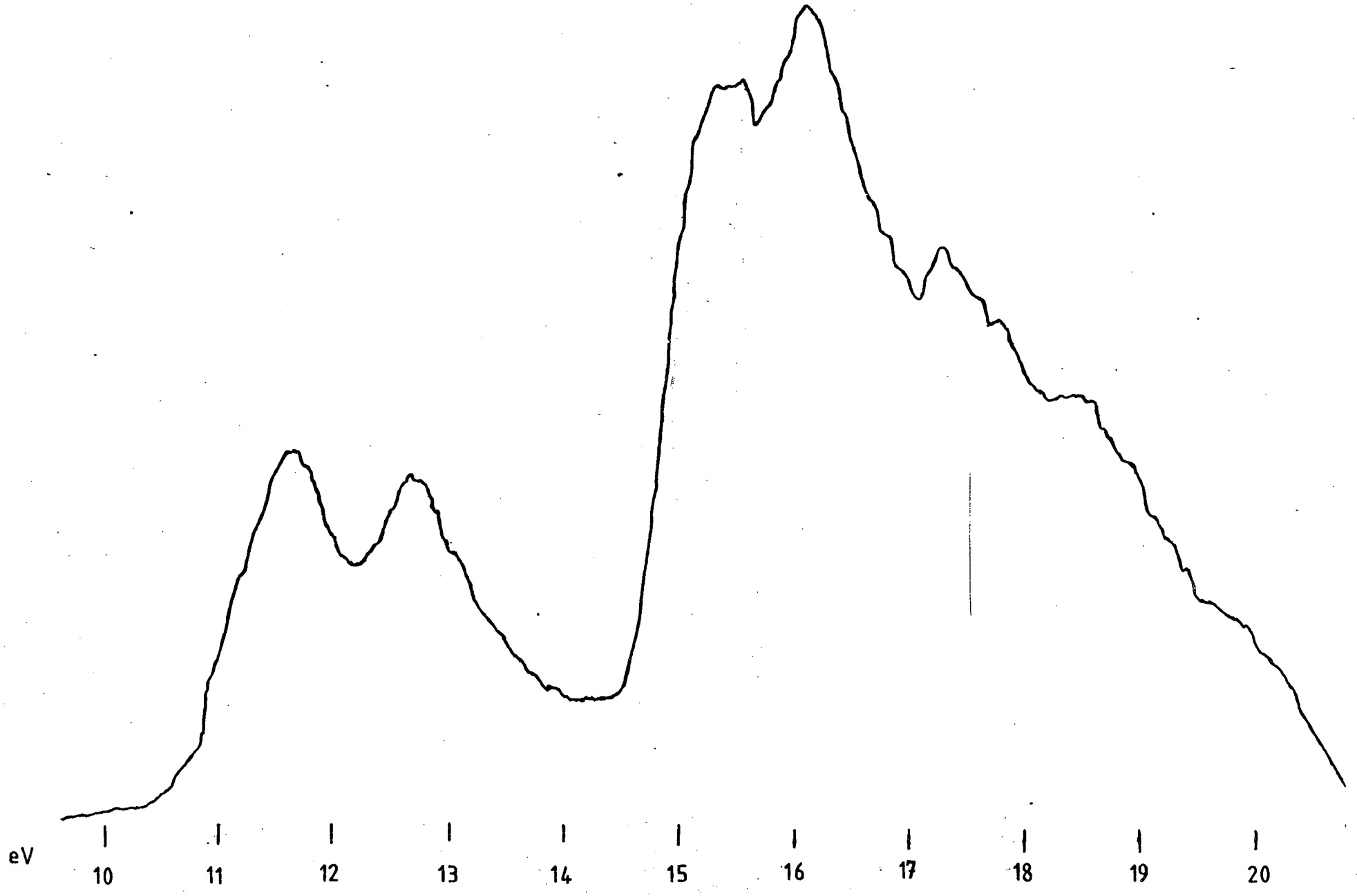
5:6 Photoelectron Spectrum

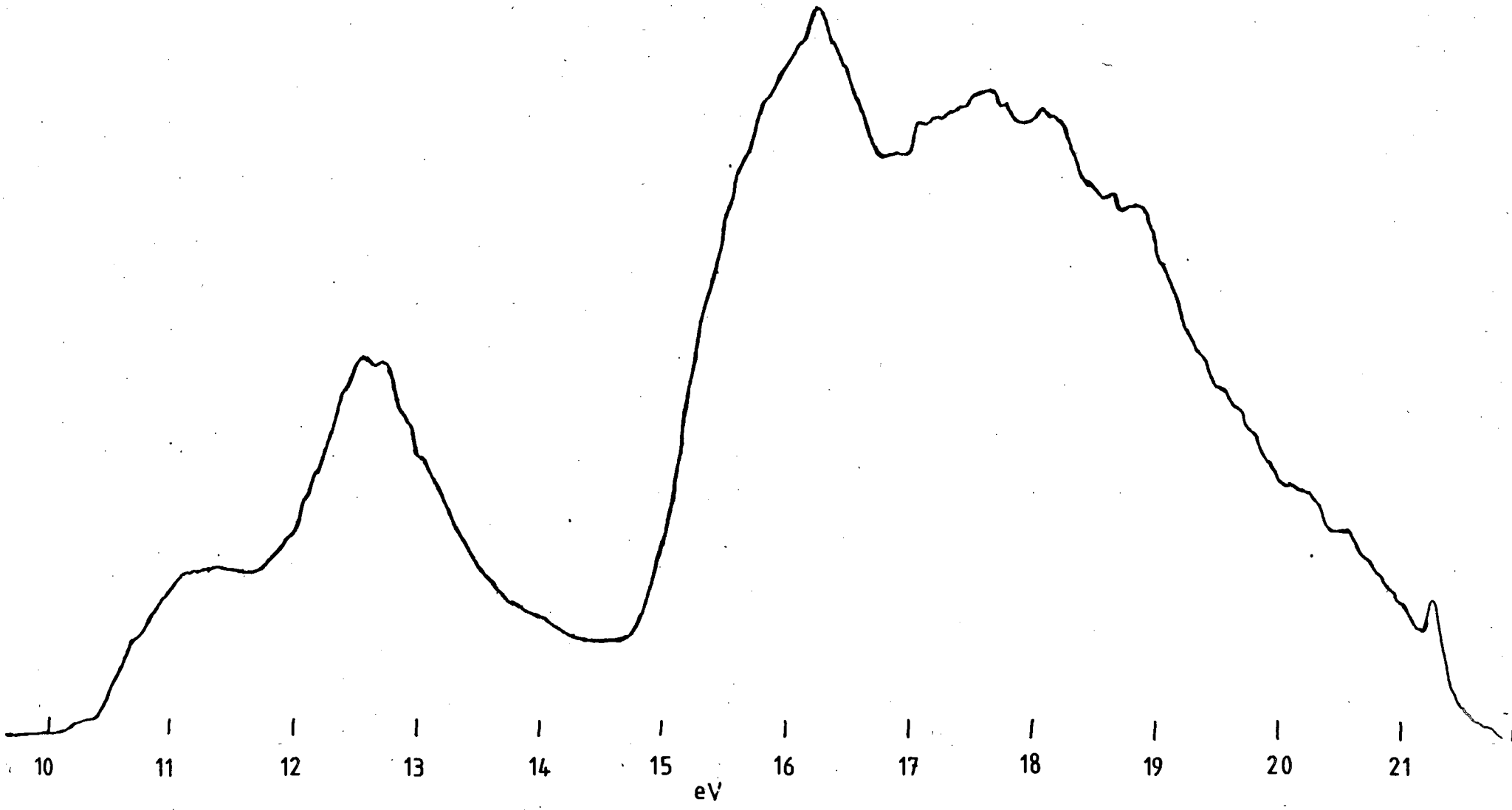
The P.E. spectra of $NH(PF_2)(PF_4)$ and $PF_2(NPF_3)$ are listed in Table 5:7. The nitrogen lone pair level, the first peak in both spectra, is at greater ionisation potential, particularly for $NH(PF_2)(PF_4)$, than in other related aminofluorophosphines[35,84] (cf. $PF_2(NH_2)$, N $2p_z$ = 10.9 eV). The phosphorus lone pair level, the second peak in each spectrum, is also shifted to higher ionisation potential. This may simply reflect the electron withdrawing properties of the $=PF_3$ and $-PF_4$ groups. The nitrogen lone pair level of $PF_2(NPF_3)$ will be mixed to some extent, due to the wide PNP angle, with the P=Nπ bonding level which is assumed to be part of the band at 12.6 eV. For $NH(PF_2)(PF_4)$, both of the P-Nσ levels, and the N-Hσ level, are assigned to the characteristic 15.55 eV band, but for $PF_2(NPF_3)$ the P-Nσ levels are unexpectedly high, and this must be associated with the exceptional molecular geometry.

5:7 Other Mixed Valency Compounds

With the preparation of $NH(PF_2)(PF_4)$, attempts were made to extend this method by reacting $PF_2[NH(SiH_3)]$ with PF_2XS (X = F, Cl, I) and PF_3O, but these preparations of $NH(PF_2)(PF_2S)$ and $NH(PF_2)(PF_2O)$ failed (Experimental Section 5:3). A

Figure 3.7 UV photoelectron spectrum of $Sn(CH_3)_4$




10
11
12
13
14
15
16
17
18
19
20
21
eV

temperature of 335 K was necessary[55] to prepare $NMe(PF_2)(PF_2O)$ - equation 5:14 - and only low yields and mixtures were obtained, but the forcing conditions may have partly derived from the Me_3Si-group.

$$PF_2[NMe(SiMe_3)] + PF_3O \rightarrow NMe(PF_2)(PF_2O) + Me_3SiF \quad ...5:14$$

Here, the only reaction detected was decomposition of the $PF_2[NH(SiH_3)]$, and heating merely accelerated this (though better results might have been obtained if the thermally stabler $PF_2[NH(SiMe_3)]$ was used), and eventually only unreacted PF_2XY (X = halogen, Y = O or S) remained. It is generally accepted though, that PF_2XY compounds are less reactive than PF_5.

5:8 Reaction of $NH(PF_2)(PF_4)$ with HX (X = Cl, Br)

This reaction would be expected to result in cleavage of the P-N bonds, giving PF_2X, PF_4X, NH_4X, and, as intermediates, $PF_2(NH_2)$ or $PF_4(NH_2)$. However, only mere traces of PF_2X were formed, and unreacted $NH(PF_2)(PF_4)$ was still present after 30 minutes in the presence of a large excess of HBr, whereas $PF_2(NH_2)$ reacts almost instantly[32], and reaction with HX is almost a diagnostic test for a P-N bond[31] (though $NH(PF_2)_2$ does not react with HBr either[35]).

The best interpretation of these results is that instead of cleaving a P-N bond, HX forms an adduct slowly, as white solids were formed. This may simply be an amine-acid adduct, or might perhaps involve a P^VX^- ion, as PF_6^- is well known. The decomposition of $NH(PF_2)(PF_4)$ has an apparent stoichiometry that suggests the formation of $NH(PF_2)(PF_4).HF$. Slow cleavage of the

P-N bond might be occurring in these adducts to account for the traces of PF_2X found, therefore the solids formed would be mixtures and analysis would not be helpful.

Cohn[163] mentions "difficulties" in the preparation of PF_4Cl from $PF_4(NMe_2)$ and HCl in the condensed phase, but does not elaborate. Perhaps here too an adduct was formed, reducing the yield of PF_4Cl and upsetting analyses.

5:9 Other Reactions

It was hoped that PF_5 and $N(SiMe_3)_3$ would react according to equation 5:14, and these products might then be reacted with

$$PF_5 + N(SiMe_3)_3 \rightarrow PF_4[N(SiMe_3)_2] + Me_3SiF$$
$$\hookrightarrow N(PF_4)_2(SiMe_3) \rightarrow N(PF_4)_3 \quad \ldots 5:15$$

P^{III} fluorides to give other $P^{III}_{NP}{}^{V}$ species. But no reaction occurred; even an hour at 355 K failed to produce any trace of Me_3SiF (Experimental Section 5:5).

This is very surprising, for PF_5 reacts with $PF_2[NMe(SiMe_3)]$[55], $PF_2[N(SiMe_3)_2]$[146], $NMe(SiMe_3)[NMe(SiMe_3)]$[177], and various $NR_2(SiMe_3)$ (R = alkyl) compounds[178], eliminating Me_3SiF quite readily. This amine's failure to react with PF_2Br was noted in Chapter 2, and the two possible explanations for this failure, and the non-reaction of $N(SiH_3)_3$ and PF_2Br[47] - steric hindrance and stabilisation by $(p\rightarrow d)\pi$ bonding - were discussed then. It is interesting at this point to examine the reaction of PF_5 with $N(SiH_3)_3$, originally studied by Milne[179], and duplicated less thoroughly by Marcus and Van Dyke[180]. Here, the less sterically congested amine does eliminate SiH_3F, but fluorination

of Si-H bonds also occurs, as do intramolecular elimination reactions (equations 5:16 and 5:17). The $N(PF_4)(SiH_3)_2$ assumed to be the intermediate was never observed however.

$$PF_5 + N(SiH_3)_3 \rightarrow N(SiH_3)_2(SiH_2F) + PF_4H$$
$$\rightarrow [N(PF_4)(SiH_3)_2] + SiH_2F_2 \qquad \ldots 5:16$$
$$\rightarrow PF_3(NSiH_3) + SiH_3F$$

$$PF_5 + N(SiH_3)_3 \rightarrow [N(PF_4)(SiH_3)_2] + SiH_3F$$
$$\rightarrow PF_3(NSiH_3) + SiH_3F \qquad \ldots 5:17$$
$$\rightarrow (NPF_2)_n + SiH_3F$$

Chapter 6

Preparation and N.M.R. Spectra of $PF_2H_2(NH_2)$

"Beware that you do not lose the
substance by grasping at the shadow"
Aesop, "Fables".

Intorduction

Several attempts at oxidative addition to P^{III} compounds to give P^{V} ones have been reported in this work, using sulphur as the oxidising agent, but these failed as the high temperature necessary for reaction[145] decomposed the starting materials (cf. Chapters 4 and 7).

Other species can also oxidise P^{III} species, the most relevant to the case in hand being NHR^1R^2 (R^1 and/or R^2 = H, Me, Et, etc.). Secondary amines with PF_2R give[22,181,182] $PFR(NR^1R^2)$ probably via oxidative addition followed by elimination of HF. Primary amines react[181,183,184] according to equation 6:1.

$$PF_2R + NH_2R \rightarrow PF_2H(NH^{\prime}R) \qquad \ldots 6:1$$

Arnold[170] extended the oxidising species to include NH_3 when excess ammonia was fortuitously used in a $PF_2(NH_2)$ preparation, giving $PF_2H(NH_2)_2$.

These earlier efforts inspired an investigation of the reaction between PF_2H and NH_3, as the product, $PF_2H_2(NH_2)$, would

be the first example of a dihydroaminofluorophosphorane. Since the expected sterochemistry of this phosphorane could lead to interesting n.m.r. and vibrational spectra, the synthesis of $PF_2H_2(NH_2)$ became doubly desirable.

The preferred axial or equatorial arrangement of the ligands can be deduced from Cavell's[185] "apicophilicity series". The fluorines will presumably take up the axial positions, being the most electronegative ligand. The orientation of the possibly planar[170] equatorial NH_2 group will be affected by F--H interactions, which will also affect several coupling constants.

The barrier to rotation about the P-N bond will be partly dependent upon these F--H interactions and it may be possible to estimate this barrier from a variable temperature n.m.r. study if the rotation can be stopped.

As the molecule may have C_{2v} symmetry, it would have been an excellent candidate for vibrational spectroscopy studies. Unfortunately, its instability has made such studies impracticable.

Results and Discussion

6:1 Preparation

The n.m.r. tube reaction of NH_3 and PF_2H - Experimental Section 6:1 and equation 6:2 - proceeded rapidly as the tube was quickly warmed to room temperature for less than one minute, and large amounts of orange-red solids were formed.

$$PF_2H + NH_3 \rightarrow PF_2H_2(NH_2) \qquad \ldots 6:2$$

Decomposition, even when recording spectra at 215 K, was a major problem but the only other product detected was PF_3. As some PF_3 was also present in the PF_2H, excess NH_3 was therefore present and this may have formed an adduct with the P^V compound, or simply acted as a decomposition catalyst.

Although the compound was unequivocally identified from its n.m.r. spectra at 215 K, attempts at actually isolating it were rather less fruitful. The liquid phase reaction of PF_2H and NH_3 - Experimental Section 6:2 - appeared to follow the same course as the n.m.r. tube reactions. Yellow solids formed at sub-zero temperatures, but the only volatile compound recovered was PF_3. Some similar solids were deposited in the traps used for fractionation, suggesting that this is a decomposition product and not the result of a side reaction.

This appears to be the least stable compound reported in this thesis, but this instability is characteristic of dihydrido - phosphorus V compounds. The decomposition of PF_3H_2 is complete at room temperature within 1 hr.[186], the compound being unstable when in contact with pyrex, and the substitution of an NH_2 group for a fluorine can only worsen matters. For it is generally accepted that the less electronegative the groups bound to phosphorus the less stable the molecule will be, demonstrated by the decrease in stability[186,187] from PF_5 to PF_4H to PF_3H_2 to PF_2H_3 and the failure to isolate PFH_4 and PH_5. Similarly, $PF_2H_2(OR)$ (R = Me, Et) and $PF_2H_2(SEt)$ were also found to be very unstable[188].

In the preparation of PF_3H_2, heating the solids which were formed liberated PH_3 and it was concluded that these solids were polymeric phosphorus sub-hydrides. However here no volatiles were produced on heating the solids to ca. 345 K for 20 minutes and it seems more likely that this reaction's solids are polymeric P-N compounds.

6:2 N.M.R. Spectra

The variable temperature study was abandoned due to the phosphorane's instability, but the molecule was stereochemically rigid at 215 K (and 223 K) on the n.m.r. timescale. Rotation about the P-N bond was also slow and the molecule had the conformation of Figure 6:1. Evidence for this comes from the second order ^{19}F and (amino) proton spectra, for only this conformation demands that the spin system be an $[AX]_2G_2MQ$ type, with the nuclei as designated in the diagram.

Although $PF_2H(NH_2)_2$, from its n.m.r. spectra[170], was apparently rigid at room temperature, rotation about the P-N bonds was occurring, making the amino protons equivalent. Though some changes were just beginning to become evident at 223 K, this rotation could not be sufficiently slowed up to make these protons inequivalent. But with only one NH_2 group in $PF_2H_2(NH_2)$, the F--H interactionswhich increase the barrier to rotation will be stronger than when shared between two NH_2 groups thus accounting for the relative ease with which P-N bond rotation was slowed up here.

For several amino phosphoranes, e.g. $PF_4(NH_2)$, the barrier to Berry pseudorotation has been calculated to be high due to P-N π interactions[189], and also to increase as the number of electronegative groups on the phosphorus atom decreases. Add to this the restraining F--H interactions and it is not surprising that $PF_2H_2(NH_2)$ is stereochemically rigid at a relatively high temperature (cf. PF_4H and PF_3H_2 where a temperature of 150 K was required to stop ligand exchange[190,191]).

The ^{31}P, ^{15}N and $P\underline{H}_2$ protons have first order spectra. The only couplings not resolvable were $^3J_{HH'}$, $^2J_{H'H''}$ and $^2J_{FF''}$. The spectra are illustrated in Figures 6:2, 6:3 and 6:4, and the

Figure 6:1 The likely structure, and spin labelling, of $PF_2H_2(NH_2)$

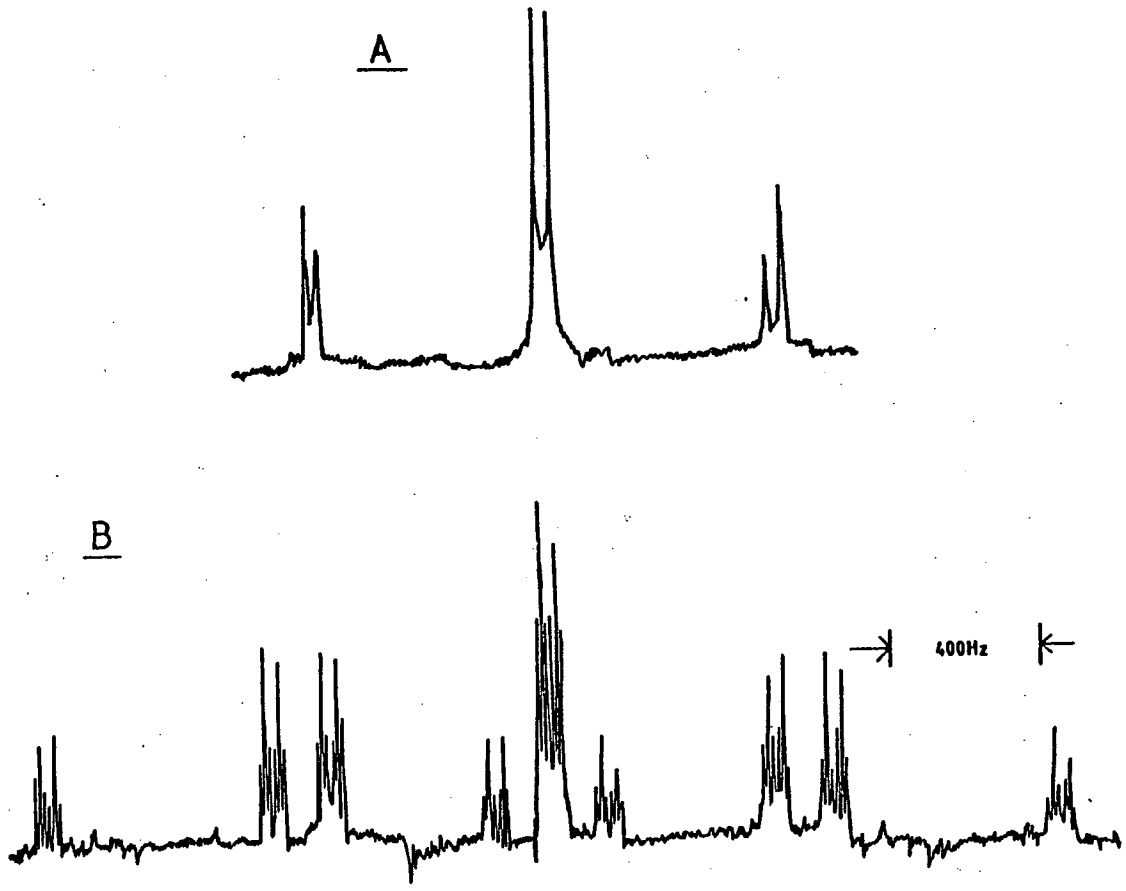


Figure 6:2 ^{31}P n.m.r. of $PF_2H_2(^{15}NH_2)$.

A. A triplet of doublets, as ^{1}H decoupled (inefficient decoupling produces the slight distortion which is evident).

B. A triplet of triplets of doublets of triplets (no decoupling).

TABLE 6:1 N.m.r. Parameters of $PF_2H_2(^{15}NH_2')$ and analogous species

Parameter	$PF_2H_2(^{15}NH_2')$	$PF_2H(^{15}NH_2')_2$	PF_4H	PF_3H_2	$PF_2H[NH'(CH_3)_2]$	$PF_4(^{15}NH_2')$	$PF_4[NH'(CH_3)]$	$PF_3(^{15}NH_2')_2$
Temp. (K)	215(a)	273	133	183	298	298	193	233
δH	+6.90	7.23	7.0	7.1	6.5			
$\delta H'$	$\sim 2.05 \pm 0.05$	2.89			3.2	n.o.	3.3	3.14
δF_{axial}	-57.46	-51.2	-27.4	-31.0	-62	-56.7	-60, -70(b)	-51.3
δP	-57.29	-63.4	-53.6	-24.1	n.o.	n.o.	n.o.	-58.6
$^1J_{PH}$	754.4	+836.0	1115	865	837			
$^1J(PF_{ax})$	598.6	-619.1	941	n.r.(c)	655	760	775, 770(b)	665
$^1J(^{15}NH')$	$\sim 88 \pm 2$	-85.0			n.o.	90.3	n.o.	87.5
$^1J(P^{15}N)$	41.1	-45.0			n.o.	n.o.	n.o.	-81.5
$^2J(F_{ax}H)$	89.6	+109.1	148	105	118			
$^2J(F_{ax}{}^{15}N)$	13.2	-14.0			n.o.	23.8	n.o.	n.o.
$^2J_{PH}$	13.0	+11.8			n.o.	17.7	~ 21	+14.5
$^2J(^{15}NH)$	4.7	-8.3			n.o.			
$^2J_{H'H''}$	<1	n.r.				n.o.		n.o.

continued

$^2J(F_{ax}F_{ax}')$	<1	n.r.				n.o.		n.o.
$^3J_{HH'}$	n.r.	<0.5						
$^3J(F_{ax}H')$	17.2	+19.7[d]			n.o.	~42[d]	27.6	1.0[e]
$^3J(F_{ax}H'')$	21.5						n.r.	41.5[e]
Reference		170	186, 190	186, 191, 192	25	175	171	117,162, 172,193

(a) Solvent $CDCl_3$/TMS//95/5

(b) Axial fluorines non-equivalent but assigned differently from those of $NH(PF_2)(PF_4)$

(c) At higher temperature, averaged $^1J_{PF}$ = 866 Hz

(d) Average of $^3J(F_{ax}H')$ and $^3J(F_{ax}H'')$

(e) At 298 K average $^3J(F_{ax}H')$ = +20.7 Hz

n.r. not resolved

n.o. not observed or studied.

parameters measured are listed in Table 6:1.

Chemical Shifts

The change in δP from +224 p.p.m. for PF_2H[195] to -57.29 p.p.m. for $PF_2H_2(NH_2)$ is the strongest evidence that oxidation to a P^V species has occurred[62,170], while δF is in the usual region[170,171,172,192]. It is difficult to make much sense of the effect on δF and δP of substituting protons or amino groups for fluorines in these P^V compounds, as some contradictory trends are apparent from Table 6:1.

For the amino proton, δH is to noticeably lower frequency of most of the other molecules of Table 6:1, and appears, not surprisingly, simply to be dependent on the electronegativity of the other groups present, while δPH is typical for a phosphorane[25,170,186].

Coupling Constants

For a P^{III} species[194,195], $^1J_{PH} \sim +180$ Hz - the increase here to ca. 750 Hz is associated with the increased s character in the bond on going from P^{III} - H, where the phosphorus uses $3p^3$ orbitals, to the equatorial P^V - H, where $3s3p^2$ hybrids are used. The increased effective nuclear charge may also be important here. Similar large values for $^1J_{PH}$ are reported for the P^V compounds of Table 6:1, and are diagnostic of such species.

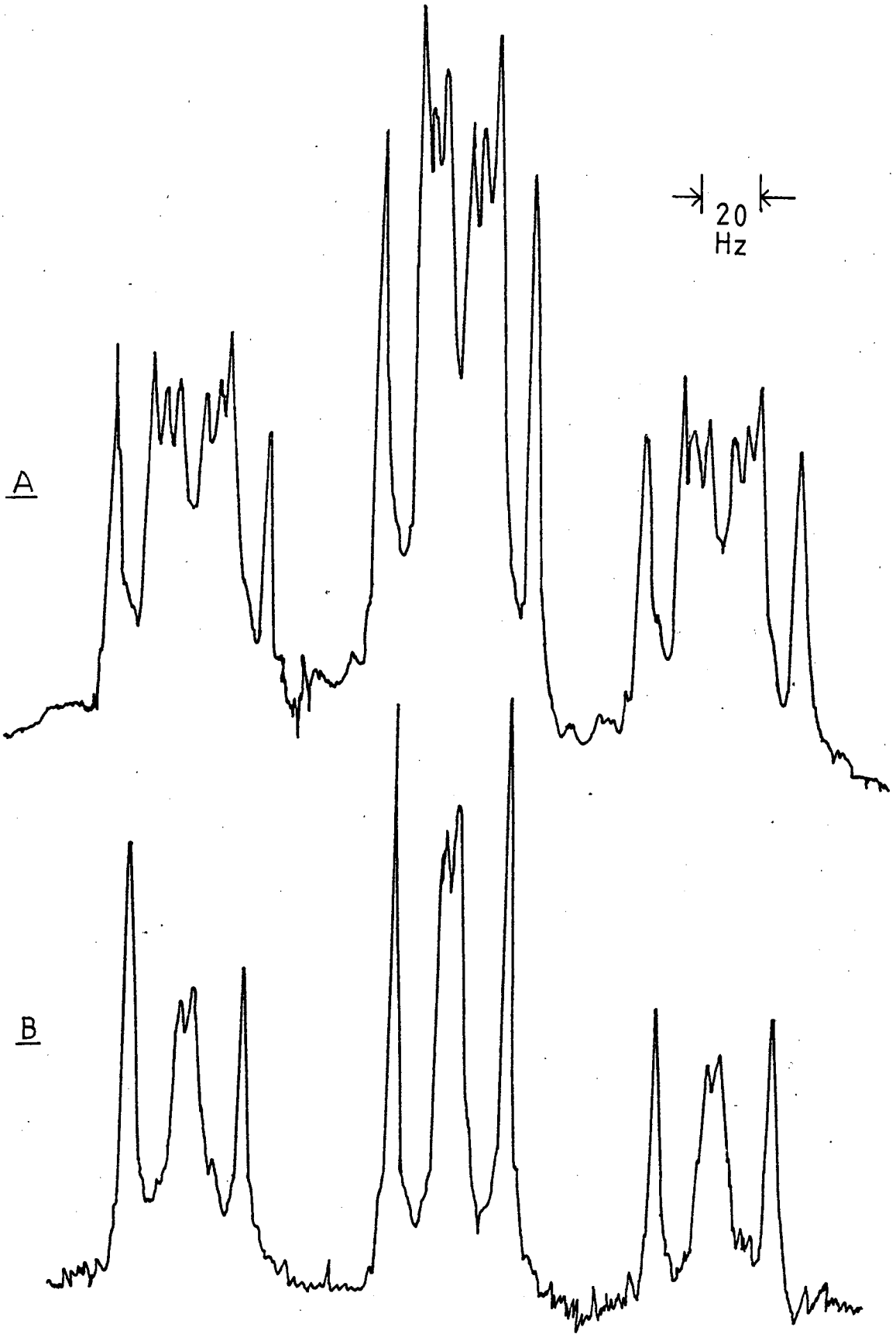
The absolute value of $^1J_{PF}$ increases with the electronegativity of the other substituents on the phosphorus, and, with two protons and an NH_2 group in the molecule, $^1J_{PF}$ here is among the smallest of such couplings reported[169,196]. This is also highly indicative that these are indeed axial fluorines, thus giving a good indication of the stereochemistry of the molecule.

Another very useful way of distinguishing between axial and equatorial fluorines in this type of molecule is by $^2J_{FH}$[190,191,197]. The usual range of $^2J(F_{ax}H_{eq})$ = 95 - 140 Hz, which is distinctly different from the much smaller values encountered for $^2J(F_{eq}H_{eq})$ = 20 - 40 Hz, and the coupling here is obviously more compatible with the former range. Also clearly noticeable is the dependence of $^2J(F_{ax}H_{eq})$ on the electronegativity of the other ligands, the lower values always being reported when two hydrogens or a group less electronegative than fluorine are present.

The AA´XX´ system formed by the two fluorines and the two amino protons requires four coupling constants and up to twelve lines in both the A and X parts of the spectrum[198]. However only four lines were observed in each spectrum due to overlap - Figures 6:3 and 6:4 - and only $^3J_{FH'}$ and $^3J_{FH''}$ could be calculated, though the maximum values of $^2J_{FF'}$ and $^2J_{H'H''}$ which would still not make the other lines resolvable were estimated. That the spectra are second order and not just doublets of doublets is obvious from the shape of the two central lines of each group of four. Although $^3J_{FH'}$ and $^3J_{FH''}$ are similar to some of those in Table 6:1, the difference between the couplings is nowhere near as pronounced as in $PF_3(NH_2)_2$ or $NH(PF_2)(PF_4)$ (cf. Chapter 5). As in $NH(PF_2)(PF_4)$ the larger coupling was assigned to the F-H pairs trans to each other. The small value implied for $^2J_{FF'}$ is in line with that found in $NH(PF_2)(PF_4)$, and also no mention[172] is made of this coupling, or $^2J_{H'H''}$, being observed in $PF_3(NH_2)_2$ (though neither is it mentioned that the spectra might be second order).

Using Binsch's equation[174], a large s contribution (~32%) to the N-H bond is implied by $^1J(N^{15}H)$ = 88 Hz, and as this equation seems to underestimate s character when electronegative ligands are present (cf. Chapter 5) then the planarity of the nitrogen is further supported.

Figure 6:3 ^{19}F n.m.r. of $PF_2H_2(^{15}NH_2)$. A. high frequency multiplet; B. with ^{15}N decoupling; showing second order features of AA'XX' spin system.



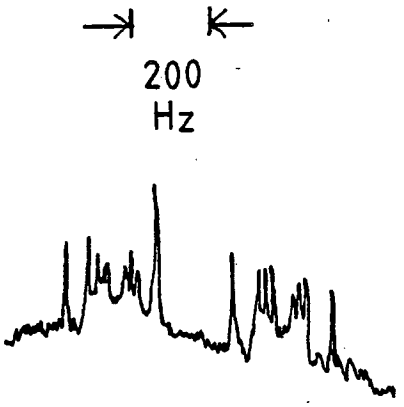


Figure 6:4 Part of ^{1}H n.m.r. of $PF_2H_2(^{15}NH_2)$ (amino protons) showing similar second order features to ^{19}F n.m.r. (Figure 6:3).

As the fluorines interact with the amino protons then a large value of $^{2}J(F^{15}N)$ is only to be expected (cf. $NH(PF_2)(PF_4)$) and is typical for fluorines in this situation[170,175]. Typically, $^{1}J(P^{15}N)$ is smaller here than in aminofluorophosphines[35,36] and the sign is in all probability negative, as opposed to positive in P^{III} species.

In conclusion there can be no doubt as to the identity or stereochemistry of $PF_2H_2(NH_2)$ from the n.m.r. data.

Chapter 7

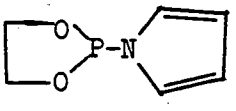
Preparation and Properties of $PF_2(NC_4H_4)$

'He paused, and then said slowly in a
deep voice: "This is the Master-ring,
the One Ring to rule them all."'

The Lord of the Rings,
J.R. Tolkien.

Introduction

The nitrogen heterocyclics are a very large class of compounds, and many of them are ripe for reaction with phosphorus halides and the potential number of PF_2N ring compounds is impressive. However, excluding molecules in which the phosphorus atom is also part of the ring system[31], only $PF(R)(NC_4H_8)$ and $PF(R)(NC_5H_{10})$ (R = F or Me), and $PF_2[N(CH_2CH_2)O]$ have been prepared[24,182,199,200]. Although organic compounds such as



have been synthesised[201], there are no reported studies of fluorophosphines attached to aromatic heterocycles - a deficiency which should obviously be rectified.

Such compounds would be interesting in that the lone pair of the nitrogen atom is involved in π-bonding with the aromatic system and will not be fully available for (p→d) π-bonding with phosphorus.

This may lead to some alterations to these compounds' properties as the resulting P-N bond must be regarded as an effectively single bond - in particular it is predicted that r P-N in these compounds will more closely approach the theoretical single-bond length than in other PF_2 amines[36,47].

The most suitable compounds for vacuum line techniques will be the simple, low molecular weight species such as pyrrole itself. The possibility of abandoning vacuum technology in favour of solutions should not, of course, be overlooked.

Results and Discussion

7:1 Preparation

The failure of Reaction 7:1 to yield $PF_2(NC_4H_4)$, and the subsequent successful preparation of this substituted heterocycle via Reaction 7:2, as described in detail in Experimental Section 7:1 and 7:2, were quite unsurprising.

$$PF_2X + HNC_4H_4 \not\rightleftharpoons PF_2(NC_4H_4) + HX \quad (X = Cl, Br) \qquad \ldots 7:1$$

$$PF_2X + HNC_4H_4 + NMe_3 \rightarrow PF_2(NC_4H_4) + [NHMe_3]X \ (X = Cl, Br) \qquad \ldots 7:2$$

Pyrrole is an extremely weak base[208] - $pK_a = -3.8$ - and does not form salts with HCl or HBr, trimerising instead[203], and so the driving force necessary for reaction is therefore absent.

However, both PF_2Cl and PF_2Br induced polymerisation of pyrrole. With PF_2Cl, a yellow solution was formed which slowly solidified over 30 minutes, the phosphine being recovered unreacted. The bromide was a very efficient catalyst, within 5 minutes a tan coloured solid formed, and only 80% of the phosphine was recovered, the rest most likely being trapped in the solid rather than incorporated into the polymer molecules.

Such polymeric pyrrole products are extremely common and are not worthy of further discussion.

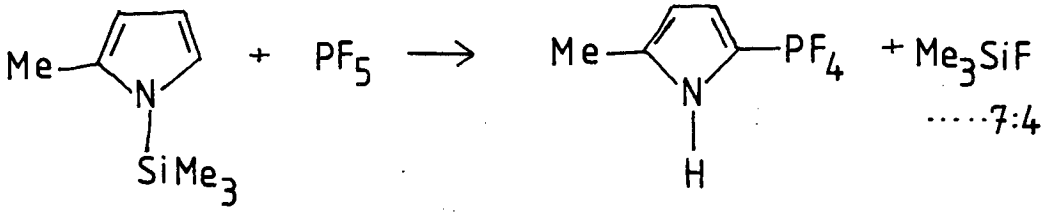
As usual, NMe_3 proved to be most efficacious in inducing the required reaction, and the preparation of $PF_2(NC_4H_4)$ was accomplished according to equation 7:2. The difference in time required for the completion of the reaction, as monitored by i.r. spectroscopy and vapour pressure, when using the bromide as opposed to the chloride reflects their known relative reactivities[31]. That both reactions give essentially the same yield, ca. 57%, is intriguing. The time difference surely rules out the decomposition of identical amounts of product and it must be concluded that some side reaction occurs. No unreacted NMe_3 was recovered, and the amounts of PF_3 obtained and PF_2X recovered accounted for approximately 25% of the phosphine initially added. Therefore equation 7:2 is not an exact description of the whole system. Purification of the product was quite simple, aided by the increase in volatility upon substitution of N-H by N-PF_2.

This compound appears to be stable, unlike the pyrrolidino derivative which undergoes disproportionation to an observable extent even at room temperature[199], equation 7:3.

$$2PF_2(NC_4H_8) \rightarrow PF(NC_4H_8)_2 + PF_3 \quad \ldots 7:3$$

An alternative route to this compound was also investigated as an extension to the studies of Si-N bond cleavage. The n.m.r. tube reaction between excess PF_2Br and $SiH_3(NC_4H_4)$ (Experimental Section 7:3) proceeded quite rapidly at ambient temperature yielding $PF_2(NC_4H_4)$ and SiH_3Br, both easily recognised from the ^1H n.m.r. spectrum. Polymerisation had also occurred giving a species encountered (but not identified) at several stages of this study, which coloured the

solution yellow. No further polymerisation had occurred even after 90 minutes though orange solids were deposited and the ratio of all the products to the residual $CHCl_3$ remained unchanged indicating that the presence of excess phosphine and SiH_3Br had not induced this polymerisation but that it was a direct by-product of the reaction. (It is worth noting the alternative route which was taken by a similar system[204], equation 7:4.)



.....7:4

However, the explosion hazard associated with silyl compounds and their tendency to hydrolyse readily make this synthesis, with the extra work of preparing $SiH_3(NC_4H_4)$[205], a less recommendable route.

That this reaction occurs, however, is interesting in itself. For it has been shown[47] that $N(SiH_3)_3$ does not react with PF_2Br, while $NH(SiH_3)_2$ eliminates SiH_3Br to form $PF_2[NH(SiH_3)]$ but not $NH(PF_2)_2$, and the non reaction of $N(SiMe_3)_3$ has already been mentioned. It is possible that stabilisation of the trisilyl compounds by (p→d) π-bonding is great enough to make any intermediate[43,44] necessary for the reaction (and the likely change in geometry associated with this) very unfavourable, while the mono and disilyl species, having less stabilisation, are more prone to attack. Furthermore, the Si-N bond in $SiH_3(NC_4H_4)$ is known to be longer than usual[206] and the π energy levels of the ring, as shown by P.E. spectroscopy[207], do not seem to be much affected by the presence of the Si atom, indicating substantially less π-bonding than usual, if any at all.

TABLE 7:1

Nuclear Magnetic Resonance Spectra of $PF_2(NC_4H_4)$

δH_α	+7.166 p.p.m.	$^1J_{PF}$	1256.9 Hz
δH_β	+6.486 p.p.m.	$^1J(P^{14}N)$	∿39 Hz (⇒$J(P^{15}N)$ ∿55 Hz)
δF	-64.57 p.p.m.	"$J(H_\alpha H_\beta)$"	2.1 Hz(a)
δP	+132.03 p.p.m.	$^3J(PH_\alpha)$	4.5 Hz
$\delta^{15}N$	n.s.	$^4J(PH_\beta)$	n.r.
δC_α	n.s.	$^4J(FH_\alpha)$	n.r.
δC_β	n.s.	$^5J(FH_\beta)$	n.r.

Solvent $CDCl_3$

Temperature 295 K

n.s. not studied

n.r. not resolved

(a) apparent splitting of "triplets", see text.

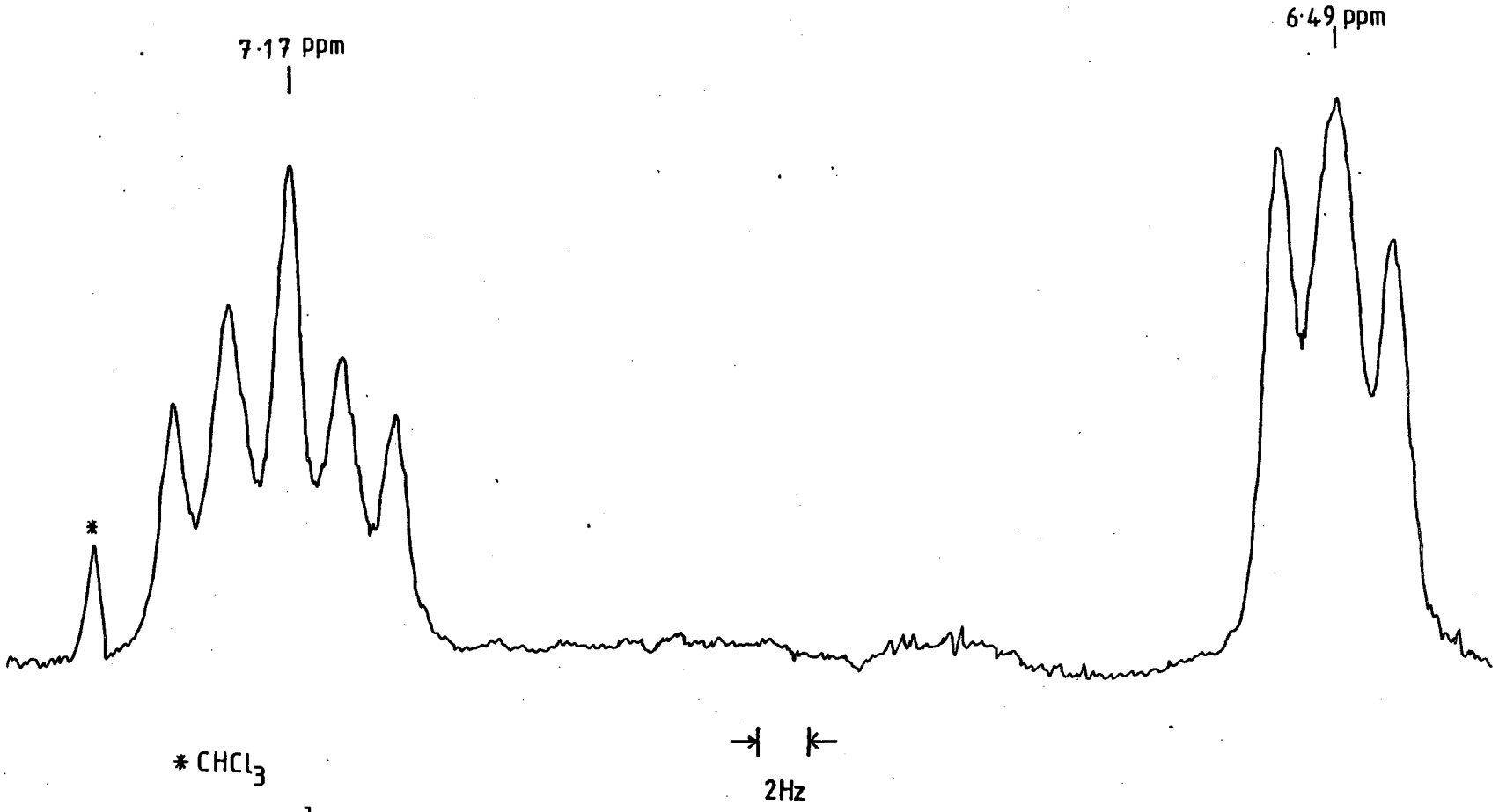
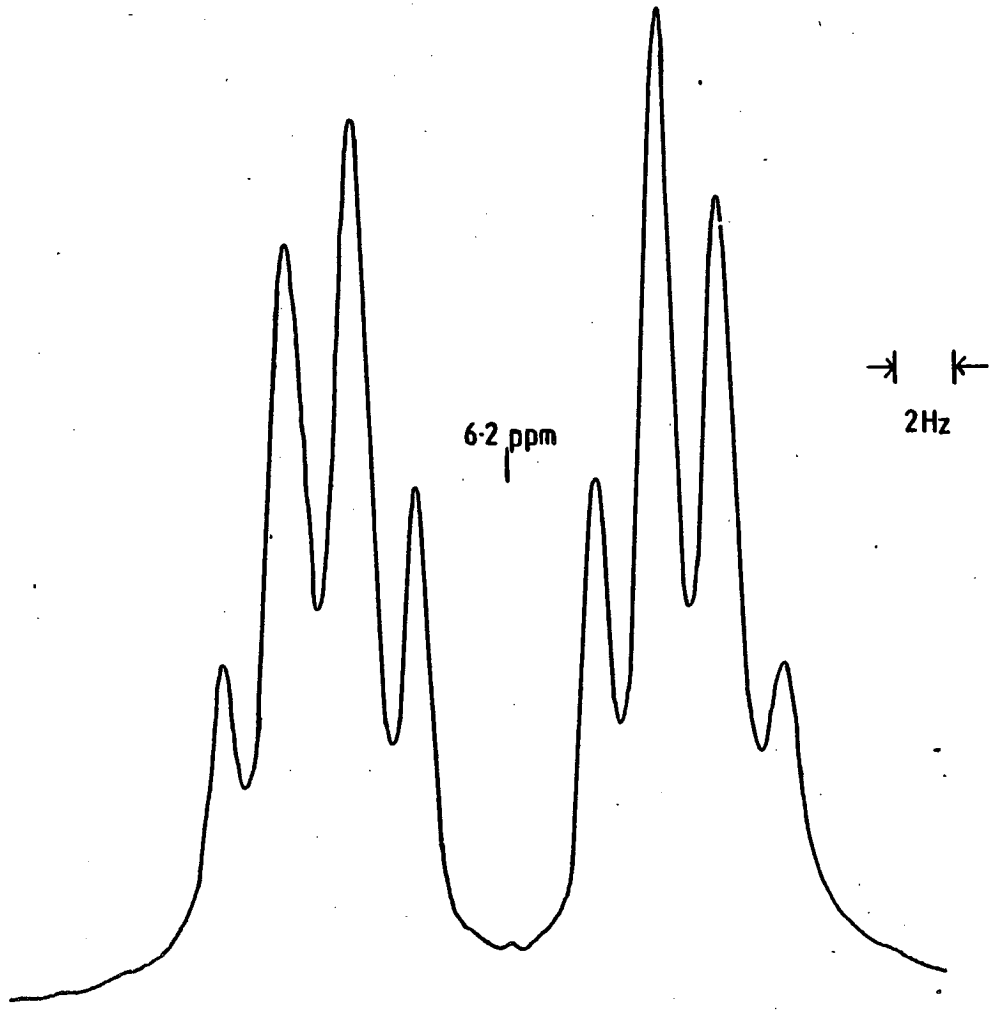


Figure 7:1 A. ^{1}H n.m.r. (60 MHz) of $PF_2(NC_4H_4)$ showing the "deceptively simple" AA'BB' pattern.

Figure 7:1 B. ^{1}H n.m.r. (60 MHz) of HNC_4H_4, another "deceptively simple" AA'BB' system.



7:2 N.m.r. Spectra

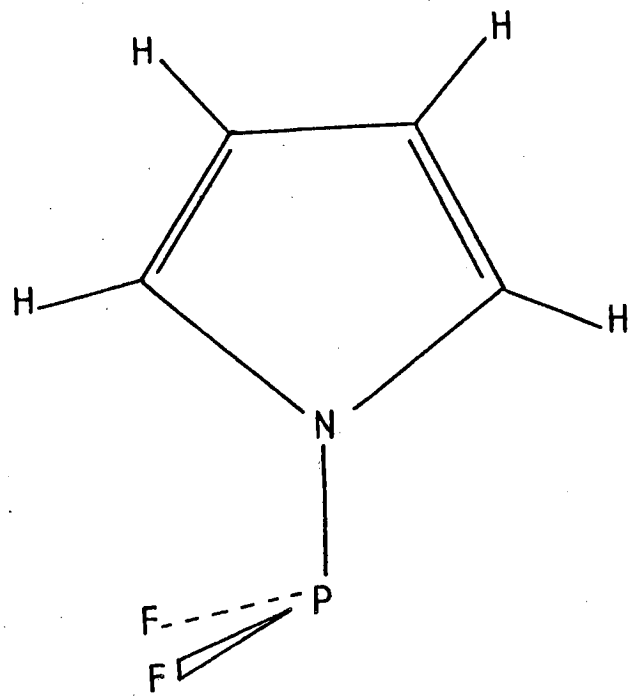
Chemical Shifts

The ^{31}P chemical shift, listed in Table 7:1 along with the other parameters, is to low frequency of those of most other PF_2 amines[31,35,36]. This is not unexpected however; the P.E. spectrum shows that the nitrogen lone pair is delocalised over the pyrrole ring and so is not available for (p→d)π bonding; this implies a different electronic contribution to the phosphorus's paramagnetic term in the chemical shift equation compared with other PF_2 amines, and this probably contributes much to the low frequency shift.

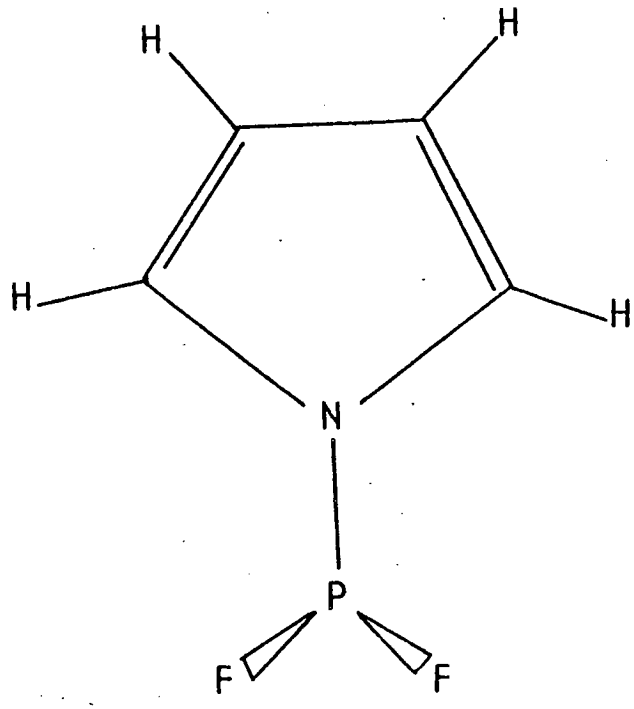
The ^{19}F shift is much less affected by this hypothetical absence of π bonding and is in the expected range[31,192]. The proton resonances are at a higher frequency than in pyrrole[208] due to the electronegativity of the PF_2 group, the α protons being affected more than the β protons due to their proximity to the PF_2 group.

Coupling Constants

While the ^{31}P and ^{19}F resonances are first order, the proton spectrum is an AA´BB´X second order spin system, but is deceptively simple[209] in that the β protons are a pseudo triplet and the α protons are a pseudo quintet i.e. a doublet (due to $^3J_{PH}$) of pseudo triplets, as shown in Figure 7:1, instead of the expected 12 lines each (excluding any coupling to the X nuclei). A similar spectrum - two "triplets" - is observed for furan[210] and this was successfully analysed due to the identification of some very weak lines close to the main triplets. This was unfortunately impossible here because of the ^{14}N broadening of the main lines obscuring these important features. (If the PF_2 group was bound to a carbon, the three ring protons would be an ABCX spin system and also couple with the resultant amino proton, which is obviously not the case).



A



B

Figure 7:2 Two possible conformations of $PF_2(NC_4H_4)$.

Double resonance experiments showed that the β protons were not coupled to either the ^{31}P or the ^{19}F nuclei, clearly due to the number of intervening bonds; and surprisingly, while the α protons couple with the phosphorus and the β protons, no coupling with the fluorine nuclei was observed yet $^{4}J_{FH}$ is usually ∿2 Hz.[25] No explanation can be suggested other than an unfavourable geometry for through space interactions, due to the ring conformation keeping the F-H distances large.

Two possible conformations for $PF_2(NC_4H_4)$ are illustrated in Figure 7:2. Conformation A requires two different $^{3}J_{PH}$'s, two $^{4}J_{FH}$'s, and an ABCD proton spin system. Conformation B only needs one $^{3}J_{PH}$, again two $^{4}J_{FH}$'s, and an AA'BB' proton spin system. Although B is closer to the observed data than A, fast rotation about the P-N bond also fits the measured parameters and as any F--H interactions in B would be too weak to hold the groups rigid, due to the large F--H distances, ∿3.5 and 4.0 Å, the rotating model is preferred.

The observation yet again of $^{1}J(P^{14}N)$ is indicative of a more symmetrical electrical field than usual around the nitrogen. The ^{31}P resonances more strongly resemble a 1:2:1 triplet than a 1:1:1 triplet, due no doubt to overlap of the peaks. Converting $^{1}J(P^{14}N)$ to $^{1}J(P^{15}N)$ (the ^{15}N isotopomer was not prepared) gives a small value for the latter for a PF_2N compound[35,36] but McFarlane[118] recently measured some similar values for $^{1}J(P^{15}N)$ in several organic compounds, and this may be typical for compounds containing N-C bonds. If the PF_2 group was bound to a carbon and not the nitrogen (cf. 2-methyl-5-tetrafluorophosphoranylpyrrole[204]) this coupling would be very much smaller, probably less than 20 Hz, and would be unlikely to be resolved. If this molecule has a planar nitrogen like pyrrole itself[202], then this is another example of the breakdown of Gray and Albright's suggestion[119,120] that the more planar the nitrogen, the larger $^{1}J_{PN}$. It would appear that a delicate balance of several factors

TABLE 7:2 Mass Spectrum of $PF_2(NC_4H_4)$

m/e	Intensity	Ion	m/e	Intensity	Ion
154	0.7	$[O(PF_2)_2]^+$	67	1.6	$[H(NC_4H_4)]^+, {}^{13}C, {}^{15}N$
136	4.6	${}^{13}C, {}^{15}N$	66	30.2	$[NC_4H_4]^+$
135	100	$[PF_2(NC_4H_4)]^+$	65	0.6	$[NC_4H_3]^+$
134	0.4	$[PF_2(NC_4H_3)]^+$	64	1.0	$[NC_4H_2]^+, [PFN]^+$
116	3.3	$[PF(NC_4H_4)]^+$	63	0.7	$[NC_4H]^+$
115	1.7	$[PF(NC_4H_3)]^+$	62	0.3	$[NC_4]^+$
113	0.7	$[PF(NC_4H)]^+$	58	0.5	$[PNCH]^+$
112	0.7	$[PF(NC_4)]^+$	52	0.3	$[C_4H_4]^+$
109	10.2	$[PF_2(NC_2H_2)]^+$	51	0.8	$[C_4H_3]^+$
108	5.9	$[PF_2(NC_2H)]^+$	50	2.4	$[C_4H_2]^+, [PF]^+$
107	1.5	$[PF_2(NC_2)]^+$	49	0.7	$[C_4H]^+$
96	9.8	$[PF_2(NCH)]^+, [P(NC_4H_3)]^+$	47	1.3	?
89	2.6	?	42	0.7	$[C_3H_6]^+$
88	1.6	$[PF_3]^+$	41	1.5	$[C_3H_5]^+, {}^{13}C, {}^{15}N$
87	0.9	$[OPF_2H]^+$	40	3.9	$[C_3H_4]^+, {}^{13}C, {}^{15}N$
86	2.2	$[OPF_2]^+$	39	26.3	$[C_3H_3]^+$

continued

85	0.5	$[PF_2(NH_2)]^+$	38	5.9	$[C_3H_2]^+$, $[C_2N]^+$
84	1.9	$[PF_2(NH)]^+$	37	3.5	$[C_3H]^+$
77	2.6	$[PF(NCH)]^+$	36	0.7	$[C_3]^+$
70	0.5	$[PF_2H]^+$	28	1.4	$[N_2]^+$, $[NCH_2]^+$
69	60.5	$[PF_2]^+$	27	1.1	$[NCH]^+$
68	0.5	$[H_2(NC_4H_4)]^+$, ^{13}C, ^{15}N	26	0.9	$[NC]^+$

Ionising potential:- 70 eV

is important as regards $^{1}J_{PN}$, and Gray and Albright do point out that a larger $^{1}J_{PN}$ would be expected for a short P-N bond, as well as some other possibly important variables.

7:3 Mass Spectrum

There are remarkably few prominent ions in the mass spectrum, recorded in Table 7:2, and the major species present corresponds to the parent ion. The main fragmentation path is simply cleavage of the P-N bond yielding $[PF_2]^+$ (m/e = 69) and $[C_4H_4]^+$ (m/e = 66). Typically, loss of fluorine atoms by the parent ion occurs but the only other route of any importance, equation 7:5, involves cleavage of a C=C bond and a C-N bond.

$$PF_2(NC_4H_4) \rightarrow \underset{m/e = 96}{[PF_2(NCH)]^+} + [C_3H_3]^+ \quad m/e = 39$$

$$[PF(NCH)]^+ + [F]^+ \qquad m/e = 77$$

$$[F]^+ + [P(NCH)]^+ \quad m/e = 58 \qquad \ldots\ 7:5$$

That m/e = 96 may represent $[P(NC_4H_4)]^+$ is admitted, but as the loss of the protons is not observed, that argument is substantially weakened. Finally, the observation of peaks corresponding to species such as $[NC_4]^+$ where the complete removal of the protons can be followed accounts for almost all the remaining peaks, and demonstrates the stability of the ring system. Reaction with traces of water is probably responsible for the oxygen-containing species.

7:4 Infra-Red Spectrum

The i.r. spectra of $PF_2(NC_4H_4)$ and HNC_4H_4 are listed in detail in Table 7:3. Using Lord and Millar's[211] analysis of the spectrum of

TABLE 7:3

Infra Red Spectra of $PF_2(NC_4H_4)$ and HNC_4H_4

HNC_4H_4	$PF_2(NC_4H_4)$		Assignments
3400			N-H str.
3133	3160	vw	C-H str.
3111	3124	vw	
3100	3128	vw	
	2535	vw	
	2471	vw	
	1763	vw	
	1730	vw	
	1581	w	
1530	1547	w	ring str.
	1540	w	
1467	1473	m	ring str.
	1462	sh	
1418	1437	w	ring str.
	1432	w	
1384	1400	vw	ring str.
	1298	w	
1237	1242	m	C-H in plane def.
	1213	s	see text
	1205	s	
1144			ring stretch
	1072	s	
1076			C-H in plane def.
1046			
	1042	m	C-H in plane def.
1015			
	982	w	

868	866	s	C-H out of plane bend
838	850	vs	C-H out of plane bend see text
	828	vs	νPF_2
	825	vs	
	787	vw	C-H out of plane def.
	780	vw	
768	734	s	"umbrella" C-H out of plane bend
711	700	vw	ring in plane bend
647	652	vw	ring in plane bend
	616	w	ring out of plane bend
	610	w	
565	557	s	ring out of plane bend
	435	w	δPF_2
	418	w	ωPF_2, $?PF_2N$ def.
	411	w	
	365	w	ρPF_2, $?PF_2N$ def.
	327	w	
	246	w	τPF_2
	226	w	
	202	w	

pyrrole and Katritzky's[212] review of substituted heterocycles, the ring vibrations can be assigned with relative confidence. A total of 9 ring vibrations are produced by a 5 membered ring containing one heteroatom which carries a substituent. (As Katritzky's review was on organic compounds, with mainly C, N or O substituents, however, the extra mass of the phosphorus may lead to some modes being at different frequencies). Ring stretching modes are assigned to bands at 1540, 1467, 1437 and 1400 cm^{-1} and the "ring breathing mode" to 1072 cm^{-1}, while the two in-plane bends are suggested as occurring at 700 and 652 cm^{-1}, with the out of plane bends at 610 and 557 cm^{-1}. These assignments compare favourably with those of pyrrole, though the last two modes are at higher frequency and the breathing mode at lower frequency than in pyrrole.

The 4 C-H stretching modes can irrefutably be assigned to the absorptions at ∿3100 cm^{-1} while the characteristic "umbrella" mode is obviously found at 734 cm^{-1}. The C-H in plane deformations are suggested as being the bands at 1242, 1067 and 1042 cm^{-1}, presumably the latter band covering 2 such modes. These assignments fit in well with pyrrole's. The remaining out of plane deformations are, with some reservations, assigned to 866, 850 and 787 cm^{-1}. These do not agree with the equivalent pyrrole modes too convincingly, and alternative assignments may be possible.

The bands allocated to P-F stretches, deformations and rocking modes are in no way exceptional, occurring at fairly characteristic frequencies. The P-N stretch however, is a bit of a problem. If as suggested several times, it is a single bond with no π contribution, a frequency of about 850 cm^{-1} would be expected[201]. This would leave the strong band at 1200 cm^{-1} unassigned, and it is possible that this is the P-N stretch coupled with a ring stretching mode.

A striking feature in the i.r. spectrum[204] of 2-methyl-5-tetrafluorophosphoranepyrrole was a strong absorption at 3450 cm^{-1} due to the N-H stretch. The absence of this band in $PF_2(NC_4H_4)$'s spectrum clearly implies that the PF_2 group is bound to the nitrogen.

7:5 Photoelectron Spectrum

The He(I) P.E. spectra of $PF_2(NC_4H_4)$ and HNC_4H_4[213] are depicted in Figure 7:3, and the assignments are listed in Table 7:4. The similarities between the two spectra indicate that no disruption of the ring π system has occurred, implying that the pyrrole ring has retained its aromaticity, and that little $(p\rightarrow d)\pi$ bonding occurs in this molecule.

Below 12 eV, the obvious similarities and differences between the spectra make assignments relatively straightforward. The two lowest energy bands are C-C π bonding levels, while the 11.2 eV band is the phosphorus $3p_z$ lone pair. The C-Cπ levels are shifted to higher eV by the stabilising effect of the electron withdrawing PF_2 group, but the difference between the two levels remains the same as in pyrrole. The presence of these two bands and this identical difference in energy clearly shows that little $(p\rightarrow d)\pi$ bonding can be occurring, especially as no nitrogen $2p_z$ electrons are observed.

The rest of the spectrum is a series of overlapping bands and, by analogy with pyrrole, we can expect the first set of bands, peaking at 13.25 eV to be C-C and C-Hσ, and C-C and C-N π levels. Above this at about 14.10 eV come the other C-Hσ levels. The broad hump at 14.65 eV is most likely the C-Nσ level with the P-Nσ level hidden under it, presumably the shoulder at ca. 15.55 eV. The F $2p_\pi$ and P-Fσ levels occur at their expected values. None of the peaks showed vibrational fine structure, unlike those in pyrrole's spectrum.

TABLE 7:4

Photoelectron Spectra

Ionisation Potential (eV)		
$PF_2(NC_4H_4)$	HNC_4H_4 [213]	Assignment
8.85	8.2	C-Cπ
9.85	9.2	C-Cπ
11.20		$P3p_z$
	12.6	C-Cσ
13.25	13.0	C-Cπ, C-Nπ
	13.7	C-Hσ
14.10	14.3	C-Hσ, N-Hσ
14.65	14.8	C-Nσ
15.55		P-Nσ
16.55		$F2p_\pi$
	17.5	C-Hσ, N-Hσ
18.4	18.1	C-Hσ, P-Fσ
	18.8	C-Cσ, N-Hσ
>19	22.3	C-Hσ
	23.8	C-Cσ, C-Cσ
	24	C-Nσ

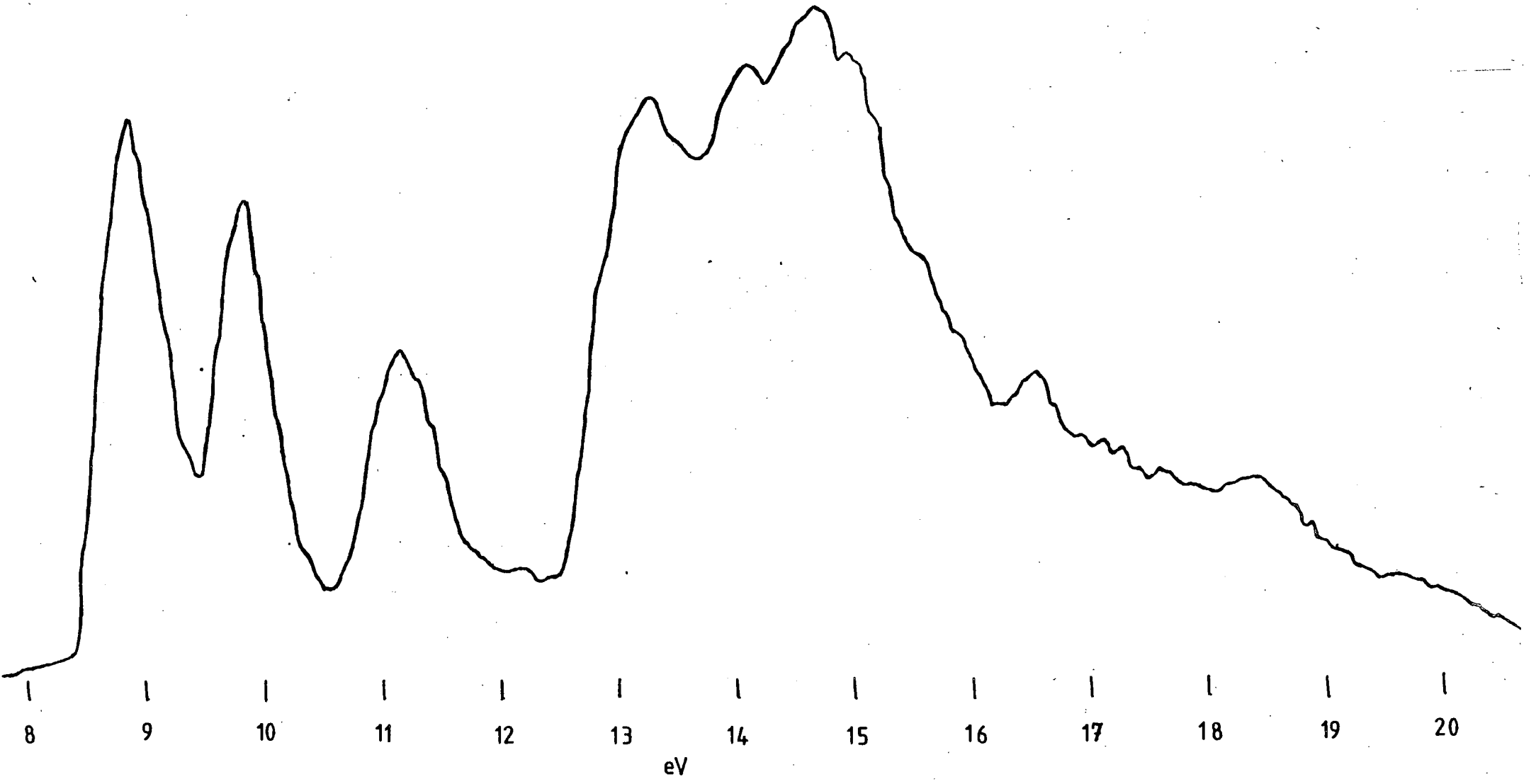


Figure 7:3 Photoelectron spectrum of $PF_2(NC_4H_4)$.

7:6 Reaction with HX

The n.m.r. tube reactions between $PF_2(NC_4H_4)$ and HX (X = Cl, Br) proceeded exactly as expected, rapidly cleaving the P-N bond, as happens with almost all PF_2N compounds[31] (notable exceptions to this rule are $NH(PF_2)(PF_4)$ and $NH(PF_2)_2$[35]). This reaction shows that the formation of an R_4N^+ salt is not absolutely necessary to drive the reaction to completion. The pyrrole produced was polymerised due to the known action of HX[203] and PF_2X, and, as described in Experimental Section 7:4, no other products were noted.

7:7 Reaction with sulphur

The oxidative addition of sulphur to tervalent phosphorus was attempted again but, as before (Chapter 4), when an n.m.r. tube containing $PF_2(NC_4H_4)$ and sulphur was heated to temperatures up to ∿355 K (Experimental Section 7:5), the phosphine decomposed, giving PF_3 (the only P or F containing molecule detected) and a polymeric compound. The sulphur remained unreacted. While it is possible that $P(NC_4H_4)_3$ could have been formed, no sign of such a compound was detected by ^{31}P n.m.r.

7:8 Borane adduct

When excess B_2H_6 was reacted at room temperature with $PF_2(NC_4H_4)$ in an n.m.r. tube, yellow solids formed and the n.m.r. spectra showed that, as is nearly always the case with phosphine - diborane reactions[150,152,154], the BH_3 adduct, $H_3B.PF_2(NC_4H_4)$, had been formed. It is not clear whether the yellow solid is just a by-product or the adduct itself, for the starting material's low volatility does not exclude the latter possibility, and some solid borane adducts are known[154]. Lack of time prevented the isolation of

the adduct to clarify this point and its identity rests entirely on the n.m.r. data. The adduct appears to be just as stable as the parent compound.

Two interesting major by-products were also identified - $H_3B.PF_3$ and $H_3B.PF_2H$. The former obviously originates from decomposition of the $PF_2(NC_4H_4)$ to PF_3, but the latter is quite fascinating for it requires the cleavage of a P-N bond presumably by the excess B_2H_6. There are two possible routes to $H_3B.PF_2H$ - equations 7:6 and 7:7.

$$H_3B.PF_2(NC_4H_4) + B_2H_6 \rightarrow H_3B.PF_2H + HNC_4H_4 + \text{a borane} \longrightarrow \text{polymer} \quad \ldots 7{:}6$$

$$PF_2(NC_4H_4) + B_2H_6 \rightarrow PF_2H + HNC_4H_4 + \text{a borane} \quad \ldots 7{:}7$$

$PF_2H \xrightarrow{\frac{1}{2}B_2H_6} H_3B.PF_2H$

$HNC_4H_4 \rightarrow$ polymer

Equation 7:6 would imply that eventually most of the product and the excess B_2H_6 would be converted to $H_3B.PF_2H$. As this is not the case, both the adduct and excess B_2H_6 still being present, equation 7:7 is preferred. The B_2H_6 probably forms a higher borane with a lower H:B ratio (B_4H_{10}, formed from "B_2H_4" + B_2H_6, fits the equation) but overlapping peaks in the n.m.r. spectrum prevented verification of this. The cleavage of P-N bonds by boranes has also been noted in the past[150]. The usual pyrrole polymer was also recognised from the spectra.

7:9 N.m.r. spectra of the adduct

Chemical Shifts

In the proton spectrum, the familiar quartet $^1J(^{11}BH)$ of pseudo quartets ($^2J_{PH} \sim {}^3J_{FH}$) at 0.89 p.p.m. due to the complexed BH_3 group

TABLE 7:5

Nuclear Magnetic Resonance Spectra of $H_3^{\prime}B.PF_2(NC_4H_4)$

δH_α	+7.11 p.p.m.	$^1J_{PF}$	1228.5 Hz
δH_β	+6.50 p.p.m.	$^1J_{BH}$	~106 Hz
$\delta H'$	+0.89 p.p.m.	$^1J(P^{14}N)$	n.r.
δF	-69.61 p.p.m.	$^1J(P^{11}B)$	56.2 Hz
δP	+123.95 p.p.m.	$^2J_{PH'}$	19.4 Hz
		$^3J_{FH'}$	17.6 Hz
		$^JPH_\alpha$	*
		$^JPH_\beta$	*
		$"J_{H_\alpha H_\beta}"$	*

solvent $CDCl_3$

temperature 295 K

n.r. not resolved

* see text and Figure 7:4

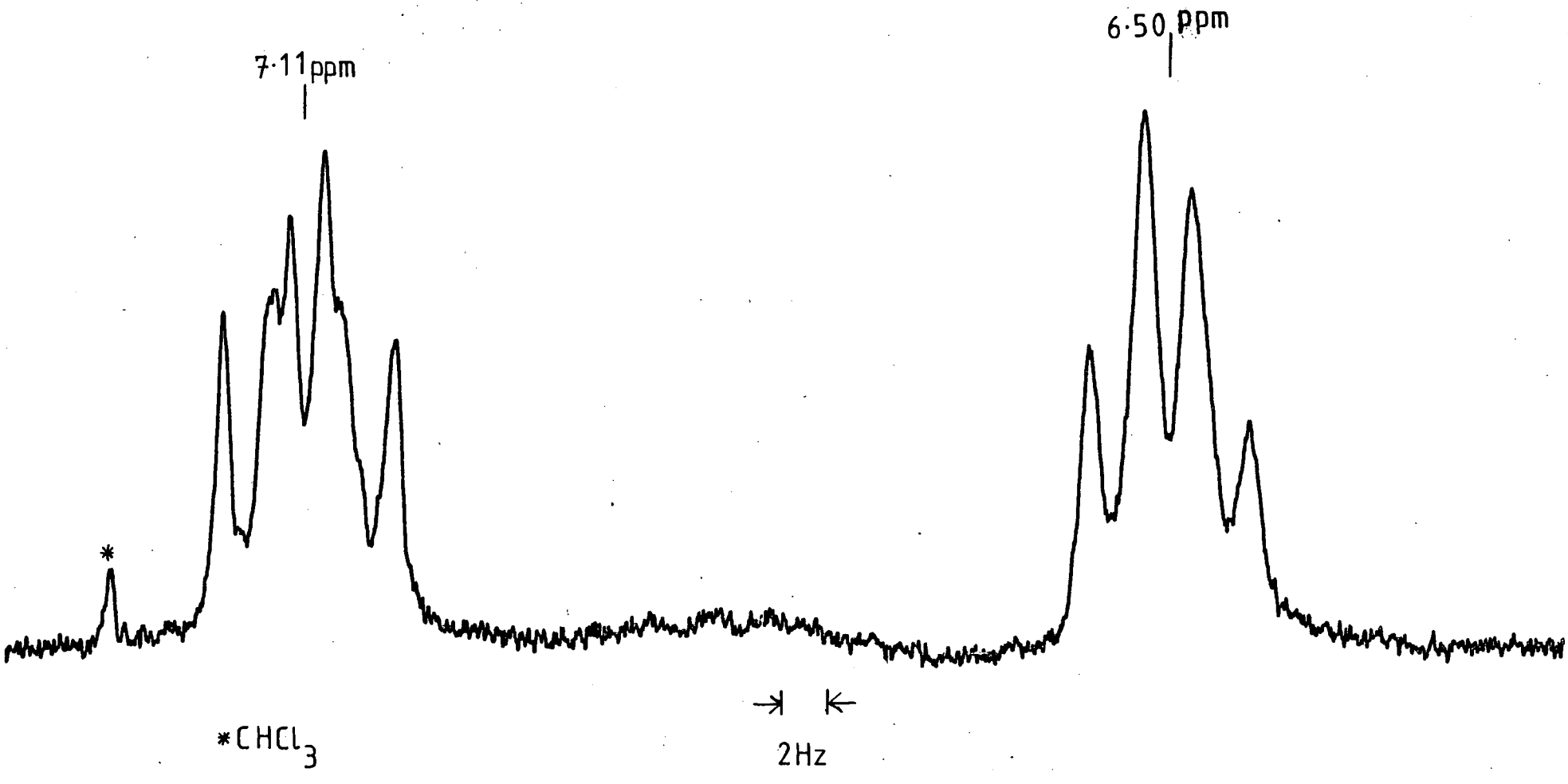


Figure 7:4 ^{1}H n.m.r. (60 MHz) of the ring protons of $H_3B.PF_2(NC_4H_4)$, showing the second order features.

was easily recognised. As was pointed out in the case of $H_3B.PF_2[N(SiH_3)_2]$, a pair of very similar borane adducts may have their basicity related[152] by $\delta B\underline{H}$ and the higher value here indicates that $PF_2(NC_4H_4)$ is a weaker base than $PF_2[N(SiH_3)_2]$, implying a lesser electron density on the phosphorus of $PF_2(NC_4H_4)$, which is in agreement with the belief that little $(p\rightarrow d)\pi$ bonding occurs in this molecule. The ring protons' chemical shifts are relatively unmoved by adduct formation.

The usual[152,153,154] low frequency shift experienced by most phosphorus nuclei complexed to BH_3, with the unmistakable triplet ($^1J_{PF}$) of quartets $^1J(P^{11}B)$, greatly simplifies identification of the product. The low frequency shift of the fluorines is less pronounced, and this is probably attributable to the number of intervening bonds. All the chemical shift data supports the belief that a P-B rather than a B-N bond is formed.

Coupling Constants

Some of the couplings are similar to those routinely met with for BH_3 complexes[153,154,155], and into this category fall $^1J_{PF}$, $^2J_{PH'}$ and $^3J_{FH'}$, while $^1J(P^{14}N)$ was not resolvable in the adduct unlike in the parent compound. As usual $^2J(F^{11}B)$ was also not observed.

There have been a few attempts[152,154,155] to correlate $^1J(P^{11}B)$ and $^1J(^{11}BH')$ with the basicity of the phosphine for smoothly varying series of complexes. Thus the quite low values observed for this adduct complement the conclusion drawn from $\delta B\underline{H}$ as regards the suggested low basicity of $PF_2(NC_4H_4)$, but the limitations of this theory, discussed in Chapter 4, should be borne in mind.

Boron decoupling greatly improved the ill-defined resonances of the BH_3 protons, clearly resolving $^2J_{PH'}$ and $^3J_{FH'}$ and also improved the ring protons signals slightly. However, the second order nature of the latter, Figure 7:4, again defied analysis. The signals resemble two sets of doublets (J_{PH} ?) of pseudo triplets but the splittings do not measure up exactly (though the discrepancies are similar to the experimental error, ~0.2 Hz). The symmetry of the proton spectrum implies that the PF_2 group is still bound to the nitrogen. All the couplings are in agreement with the proposed formulation.

Chapter 8

Derivatives of Acetamide Containing PF_2-groups

"The Universe is not only queerer than we imagine,
it is queerer than we can imagine".

Professor J.B.S. Haldane.

Introduction

Apart from amines, nitrogen forms other classes of compounds with N-H bonds which therefore might be reacted with PF_2Br to give new types of $F_2P\text{-}N<$ compounds. So far, no work has been published on amides and so they were deemed worthy of investigation. The synthesis was attempted of only the simplest compounds i.e. $PF_2[NH(CO(CH_3))]$ and $N[CO(CH_3)](PF_2)_2$, and the first attempts involved variations on the synthesis of $PF_2(NH_2)$ and its derivatives[32,36]. However, as shown by the reaction of $SiH_3(NC_4H_4)$ with PF_2Br (Chapter 7), an N-H bond is not a prerequisite for the synthesis of $F_2P\text{-}N<$ compounds. In fact two quite separate approaches to acetamide derivatives were undertaken and these are now considered separately. However, lack of time, and separation and volatility problems prevented the complete characterisation of any of the compounds of this chapter.

8:1 Synthetic Routes Analogous to those of $PF_2(NH_2)$ and $PF_2[NH(SiH_3)]$

Results and Discussion

8:1A Preparation of $PF_2[NH(CO(CH_3))]$

In an attempt to prepare $PF_2[NH(CO(CH_3))]$ by an analogous route to that used [36] for $PF_2[NH(SiH_3)]$ and the other silyl and germyl

amines, $PF_2(NH_2)$ and $CH_3CO.Cl$ were reacted, with and without the presence of NMe_3, Experimental Sections 8:1 and 8:2.

$$3PF_2(NH_2) + 2CH_3CO.Cl \rightarrow 2PF_2[NH(CO(CH_3))] + PF_2Cl + NH_4Cl \quad ...8:1$$

$$PF_2(NH_2) + CH_3CO.Cl + NMe_3 \rightarrow PF_2[NH(CO(CH_3))] + Me_3NHCl \quad ...8:2$$

In each case a white solid which later turned yellow was formed, but fractionation only afforded mixtures of starting materials, as shown by i.r. spectroscopy, with no traces of the expected products being observed. Although these reactions may be assumed to be failures, the nature of the solid remains a mystery. Perhaps it is an adduct of some sort. Perhaps these experiments should have been repeated in an n.m.r. tube where the solids may be dissolved, as it is just possible that the desired product is a solid. (Note that $CH_3CO[NH(SiMe_3)]$ is a solid but $CH_3CO[N(SiMe_3)_2]$ is a liquid[214]). A similar, successful preparation of $PF_2[NH(CO(CH_3))]$(S) has been reported, however[215].

A variation on the preparation of $PF_2(NH_2)$ was considered next. The reaction of PF_2Br and acetamide in an n.m.r. tube, Experimental Section 8:3, was, however, slightly disappointing,

$$PF_2Br + 2NH_2[CO(CH_3)] \rightarrow PF_2[NH(CO(CH_3))] + CH_3CONH_3Br \quad ...8:3$$

Although copious amounts of white solid (the hydrobromide) were formed, only minute traces of the product could be detected by ^{31}P and ^{19}F n.m.r., and most of the PF_2Br was still unreacted. This anomaly, however, is explicable. Instead of dissolving in the n.m.r. solvent, the solid acetamide reacted immediately, and the surface of the finely ground clear compound became coated with

white acetamide hydrobromide thus preventing further reaction.

Water absorbed from the atmosphere is usually associated with the acetamide crystals, leading to a large number of by-products which dominate the spectra unless the sample is first finely ground then pumped on for a day on the vacuum line.

A modification which might yield significant amounts of product would be an arrangement to bubble PF_2Br through a solution of acetamide, either under vacuum or an N_2 atmosphere. Alternatively, PF_2Br under pressure could be admitted to an ampoule containing an acetamide solution and the reactants then shaken; or rapidly freeze an acetamide solution before adding the PF_2Br. The tiny yield of $PF_2[NH(CO(CH_3))]$ prevented any attempts at its isolation.

8:1B N.M.R. Spectra

Chemical Shifts

The ^1H n.m.r. of $PF_2[NH(CO(CH_3))]$ (Table 8:1) showed a doublet of triplets, due to coupling with ^{31}P and ^{19}F, at 2.15 p.p.m., assigned to the CH_3 group, and a broad hump at ca. 7.0 p.p.m. which is suggested as the NH group. Quadropolar broadening by the ^{14}N, and perhaps exchange with any water still present in the tube were probably responsible for this ill-defined signal. Broadening by ^{14}N affects the ^{31}P spectrum also and $\delta^{31}P$ is perfectly typical[31,32,35,36] for a $PF_2N<$ compound, being similar[91] to that of $PF_2[NH(CH_3)]$. Likewise δF is similar to those of $PF_2(NHR)$ compounds[25].

Coupling Constants

Only a few couplings could be resolved. While $^1J_{PF}$ was within the expected range, $^3J_{FH}$ was much smaller than usual - 4.2 Hz as opposed to 10-16 Hz for $PF_2(NHR)$ compounds[25]. If the fluorines were orientated to interact with the amine proton, then $\angle FPNH$ would

Table 8:1

N.M.R. Parameters of $PF_2[NH(CO(CH_3))]$

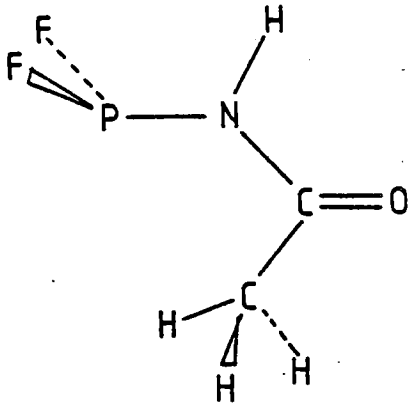
δP	+146.6	ppm
δF	-73.8	ppm
$\delta \underline{CH}$	+2.15	ppm
$\delta \underline{NH}$	~7.0	ppm
$^1J_{PF}$	1235	Hz
$^2J_{PH}$	n.r.	
$^3J_{FH}$	4.2	Hz
$^4J_{HH}$	n.r.[a]	
$^4J_{PH}$	2.4	Hz
$^5J_{FH}$	0.4	Hz

Solvent:- $CDCl_3$/TMS//95/5

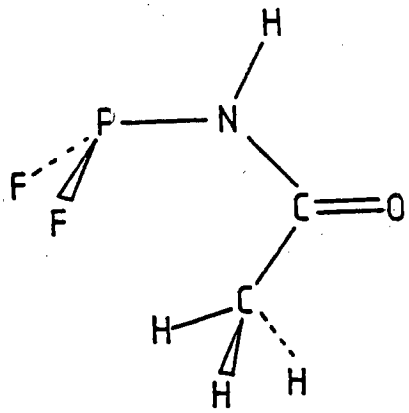
Temperature:- ambient

[a] Maximum possible value <0.2 Hz

n.r. not resolved



A



B

Figure 8:1 Two possible conformers of $PF_2[NH(CO(CH_3))]$.

The n.m.r. spectra imply conformer A is present.

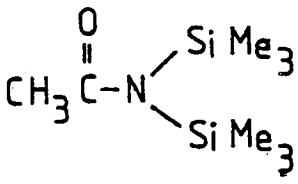
be small, and the Karplus type relationship proposed for this coupling in Chapter 5 would account for the small coupling. As $^4J_{PH}$ is significantly larger (2.4 Hz) here than in $PF_2[NH(Bu^t)]$, $PF[NH(Bu^t)]_2$, and cyclodiphosph(III)azanes, where the average $^4J_{PH}$ was 0.7 Hz[25,127], it may be deduced that the rest of the molecule is orientated to bring the CH_3 group into a cis relationship with the P lone pair (Figure 8:1) as this usually leads to larger couplings. In the cyclodiphosph(III)azanes[135,136] the lone pair is not directed towards the CH_3 group, which results in a small coupling. Few values of $^5J_{FH}$ are available, but the small value is in line with the number of intervening bonds. While ^{14}N broadening of the ^{31}P spectrum obscured $^2J_{PH}$, the coupling is probably rather small anyway, perhaps only a few hertz, due to the proposed orientation of the P lone pair trans to the amino proton.

8:2 Synthesis from Bis(trimethylsilyl)acetamide

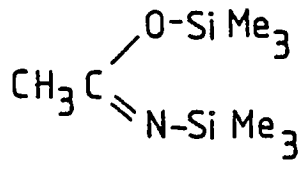
8:2A Introduction

A compound well known to organic chemists for its ability to lose Me_3Si-groups readily[214,216], bis(trimethylsilyl)acetamide (BSA) may be expected to react with PF_2Br, eliminating Me_3SiBr, resulting in easy access to PF_2-acetamide derivatives. However, there is an interesting structural feature of BSA which complicates matters.

The position of substitution of the two Me_3Si-groups has been the subject of several papers[217,218,219,220,221] presenting opposing views, sometimes even using the same data, and the two possible structures are shown in Figure 8:2. Most of the evidence favours structure II; however an equilibrium[221] between the two forms has also been suggested with II being the much more strongly favoured form. But BSA would not be unique in this respect, as equilibria



I



II

Figure 8:2 The two structures proposed for BSA.

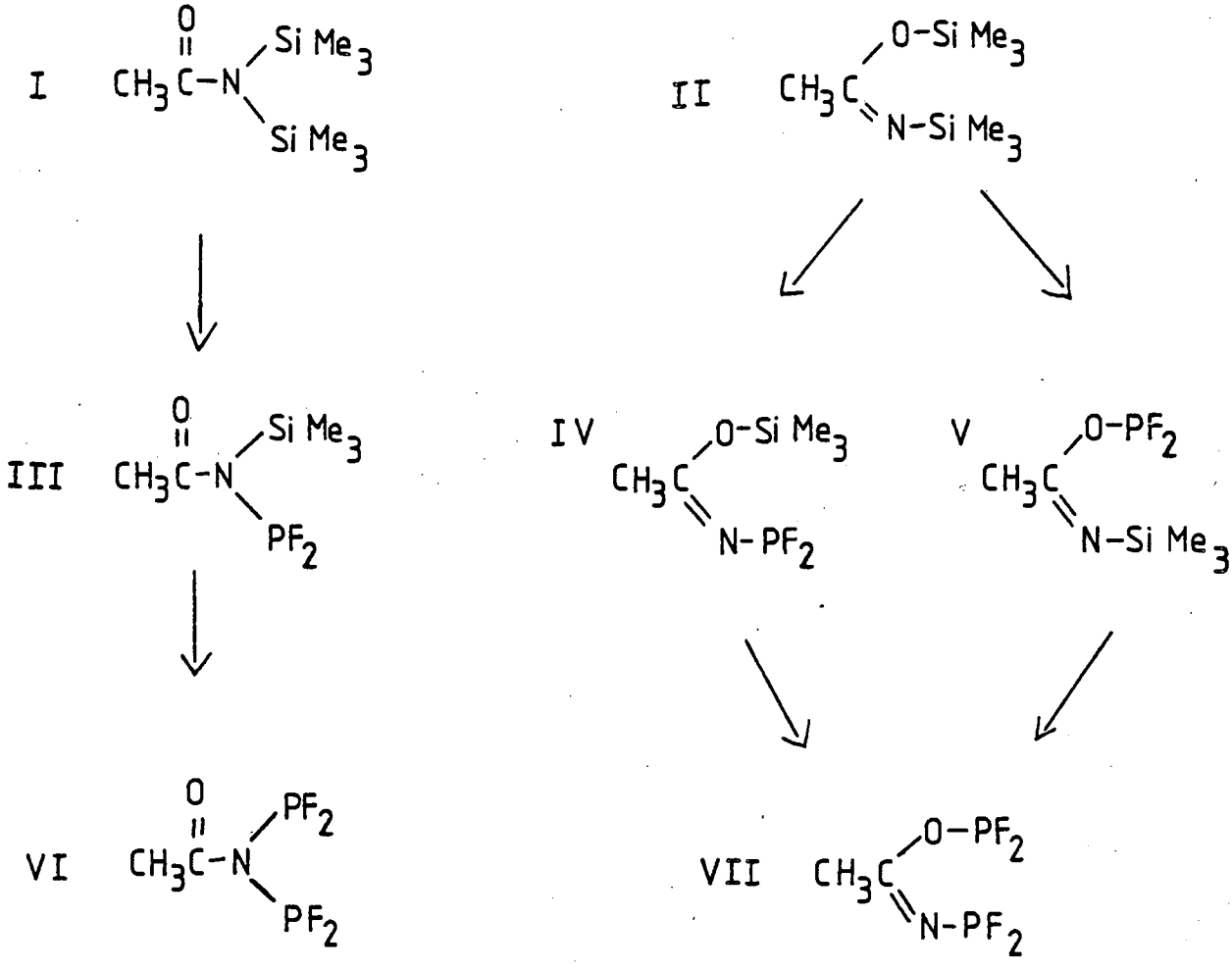


Figure 8:3 Possible products from the reaction of BSA with PF_2Br.

have been reported for e.g. $RCO[NR](SiMe_3)$[221], $ArC(NSiMe_3)(OSiMe_3)$[221], and $(PhO)_2PO[N(Ph)(SiMe_3)]$[222].

If no preconceived ideas as to which structure (if either) of BSA is the predominant form are allowed to cloud the issue, then the reaction of BSA with PF_2Br can lead to any of five possible compounds, Figure 8:3.

Results and Discussion

8:2B Preparations

When excess PF_2Br was reacted with BSA, Experimental Section 8:4, after 30 minutes at 290 K, approximately 1.5 mmoles of Me_3SiBr per mmole of BSA were recovered upon fractionation of the products. Treatment of the products with a further quantity of PF_2Br did not release more than a trace of Me_3SiBr, although the total amount of PF_2Br consumed indicated almost complete replacement of Me_3Si- by PF_2-. It always proved impossible to recover the full complement of Me_3SiBr but n.m.r. showed that the samples contained free Me_3SiBr. From the n.m.r. spectra (and the PF_2Br consumed) it was deduced that the products were $N[CO(CH_3)](PF_2)_2$ and $CH_3C(NPF_2)(OPF_2)$, compounds VI and VII. This would seem to indicate that BSA does exist as two isomers in equilibrium. (However, recent work[223] on this system has shown that if the reaction is carried out at 193 K, the only product is compound VII, and at temperatures above 233 K, this molecule slowly rearranges to give a mixture of VI and VII).

Variable temperature n.m.r. studies on the above mixture showed no line broadening in the range 208 to 333 K i.e. no evidence of an equilibrium involving PF_2 group exchange. Although not as closely examined, there was no evidence to suggest any

further change with time, or that the intermediate, mixed silyl-phosphine species undergo exchange.

The decomposition products noted were traces of PF_3 and somewhat more $O(PF_2)_2$, although the latter perhaps arises only when the products are in contact with glass which is not scrupulously dry.

If a 1:1 (or even a 2:1) ratio of PF_2Br to BSA is reacted instead of an excess, then a multitude of peaks appears in the n.m.r. spectra. After eliminating the resonances of compounds VI and VII, a comparison with literature data[224] showed the presence of $O(SiMe_3)(PF_2)$. It has now[223] been shown that this compound, and CH_3CN, are the decomposition products of what has been described here as compound III, to which the remaining peaks in the spectra were assigned. (However it has recently been suggested[223] that these peaks are due to compound IV and not III, on the basis of the i.r. spectrum of this species which apparently does not show a C=O stretching mode).

Repeating the reactions in wet solvents (Experimental Section 8:5) leads to the additional formation of $PF_2[NH(CO(CH_3))]$. Whether this was only from the above products reacting with the water, or the BSA reacting to give $CH_3CO[NH(SiMe_3)]$ which can still react with PF_2Br was not investigated, but reaction of $CH_3CO[NH(SiMe_3)]$ with PF_2Br would be worth further investigation.

Reacting the mixture of VI and VII with water gave the same products. No evidence for species such as $PF_2N(COH)(CH_3)$ or $NH(COPF_2)(CH_3)$ could be found, although they might rapidly rearrange to the $PF_2[NH(CO(CH_3))]$ observed.

8:2C N.M.R. Spectra

The spectra are summarised in Table 8:2. Second order features in the ^{31}P and ^{19}F spectra of $N[CO(CH_3)](PF_2)_2$ (VI) made it instantly recognisable, but although similar to other $[A[X]_2]_2$ patterns[96], there were some discrepancies (Figures 8:4 and 8:5) and they could not be fully analysed. Broadening by ^{14}N occurred in the ^{31}P spectra of PF_2N species.

Chemical Shifts

Although δP and δF of VI are similar to those of $PF_2[NH(CO(CH_3))]$ and $(PF_2)_2N$- species[97,121], they are both to low frequency of most of the latter compounds. Part of this difference may be due to the possible conformation which VI is likely to adopt. Interactions between the CH_3 group and one of the PF_2 groups, and steric and electrostatic repulsions between the other PF_2 group and the oxygen make Figure 8:6A the likeliest structure, with possible interactions between the fluorines and the other P's lone pair. But the spectra imply that the two PF_2 groups are equivalent (or almost so, remembering the second order pattern). This is envisaged as due to rotation about the P-N bonds which would induce a cog-wheel effect on the $N-CO(CH_3)$, with all three groups rotating synchronously, averaging δF and δP. The variable temperature ^{19}F study showed no slowing of this rotation at 208 K, but a study to lower temperatures would be justified.

For compound VII, two distinct P's and F's were observed. Although δP for the $-O-PF_2$ group was fairly typical[31], δP for the $=N-PF_2$ group was significantly higher than that[52] of $PF_2(NPF_3)$ (+129 p.p.m.), though which is the unusual chemical shift is difficult to say; however $\delta P^{III}\underline{F}$ for the latter compound is at

Table 8:2

N.M.R. Parameters of III, VI and VII

	δP ppm	$\delta P'$ ppm	δF ppm	$\delta F'$ ppm	δH ppm	$^1J_{PF}$ Hz	$^1J_{P'F'}$ Hz	$^2J_{PP'}$ / $^4J_{PP'}$ Hz	$^3J_{PF'}$ / $^6J_{PF'}$ Hz	$^4J_{PH}$ Hz	$^5J_{PH}$ Hz
$CH_3CO[N(SiMe_3)(PF_2)]$ III	+154		-65.6		n.s.	1250				n.s.	n.s.
$N[CO(CH_3)](PF_2)_2$ VI	+144.6		-70.00		+2.39	-1297.4		32.7	+34.9	4.5	0.9
$CH_3C(NPF_2)(OP'F'_2)$ VII	+149.8	+122.18	-66.40	-57.69	+2.33	1269.8	1345.1	n.r.	n.r.	n.r.	n.r.

Solvent:- $CDCl_3$

Temperature:- 293 K

n.s. not studied

n.r. not resolved

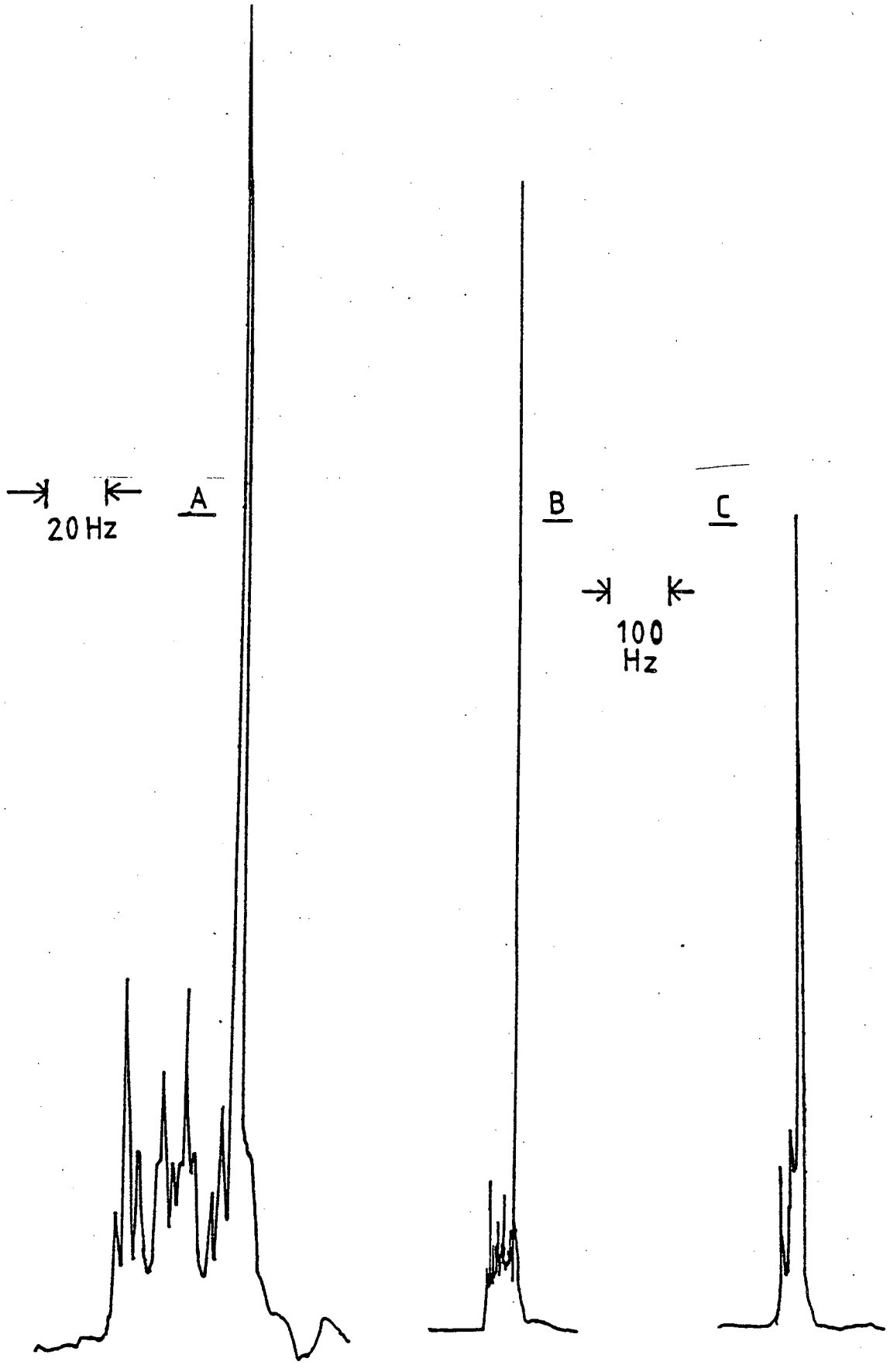


Figure 8:4 ^{19}F n.m.r. of $N[CO(CH_3)](PF_2)_2$, ^{1}H decoupled.

A. Expansion of the high frequency half, at 323K.

B. Unexpanded A, at 323K.

C. Same sample, at 208K.

unusually high frequency for a PF_2N-compound whereas for VII δF is more typical[31]. However δF for PF_2-O- is at unusually low frequency.

Quite similar values of δH are found for VI and VII. One of the resonances was a quintet (J_{FH}) of triplets (J_{PH}) while the other, although broadened, had no resolvable fine structure. The former, at δ = 2.39 p.p.m., was assigned to VI, and the latter, at δ = 2.33 p.p.m., to VII. Replacement of the $SiMe_3$ groups of BSA with PF_2 groups has moved the CH_3 resonances of VI and VII to high frequency[217].

Of the three mono-substituted isomers, only one was formed. Compound III is assigned to the signals at δP = 154 p.p.m. which is similar to that of $PF_2[NH(SiMe_3)]$ (159.6 p.p.m.), while δF is also fairly typical of a $PF_2N<$ species. It was not possible to distinguish which of the several peaks in the Me_3Si region were due to III as opposed to by-products, nor could the CH_3 group's resonances be reliably located.

Coupling Constants

Few couplings were resolved. A larger value of $^1J_{PF}$ was found for the F_2PO species than for the F_2PN species, as usually happens[31]. More interesting however is $^2J_{PP'}$ in compound VI. If the conformation of VI was analogous to that[86] of $N(CH_3)(PF_2)_2$, Figure 8:6B, the P lone pairs would interact and result in a large $^2J_{PP'}$ of about 300 Hz. Although the second-order spectra could not be fully analysed, the small $^2J_{PP'}$ = 32.7 Hz supports the belief that one PF_2 group has rotated by 180°, Figure 8:6A, thus eliminating the lone pair interactions, the other PF_2 group presumably hydrogen bonding to the CH_3 group. The small $^2J_{PP'}$ in $N(PF_2)_3$[35] implies a similar nose-to-tail arrangement of PF_2 groups,

Table 8:3

Variable Temperature ^{19}F n.m.r. Study of $N[CO(CH_3)](PF_2)_2$

Temperature (K)	$^1J_{PF}$	$^3J_{PF'}$	$^2J_{PP'}$	δF
208	-1300.9 Hz	+26.7 Hz	n.r.	-70.54 ppm
223	-1299.1	+30.9	32.9 Hz	-70.20
273	-1298.4	+33.1	32.7	-70.01
293	-1297.4	+34.9	32.7	-70.00
323	-1295.9	+37.0	32.4	-69.59

Solvent:- $CDCl_3$

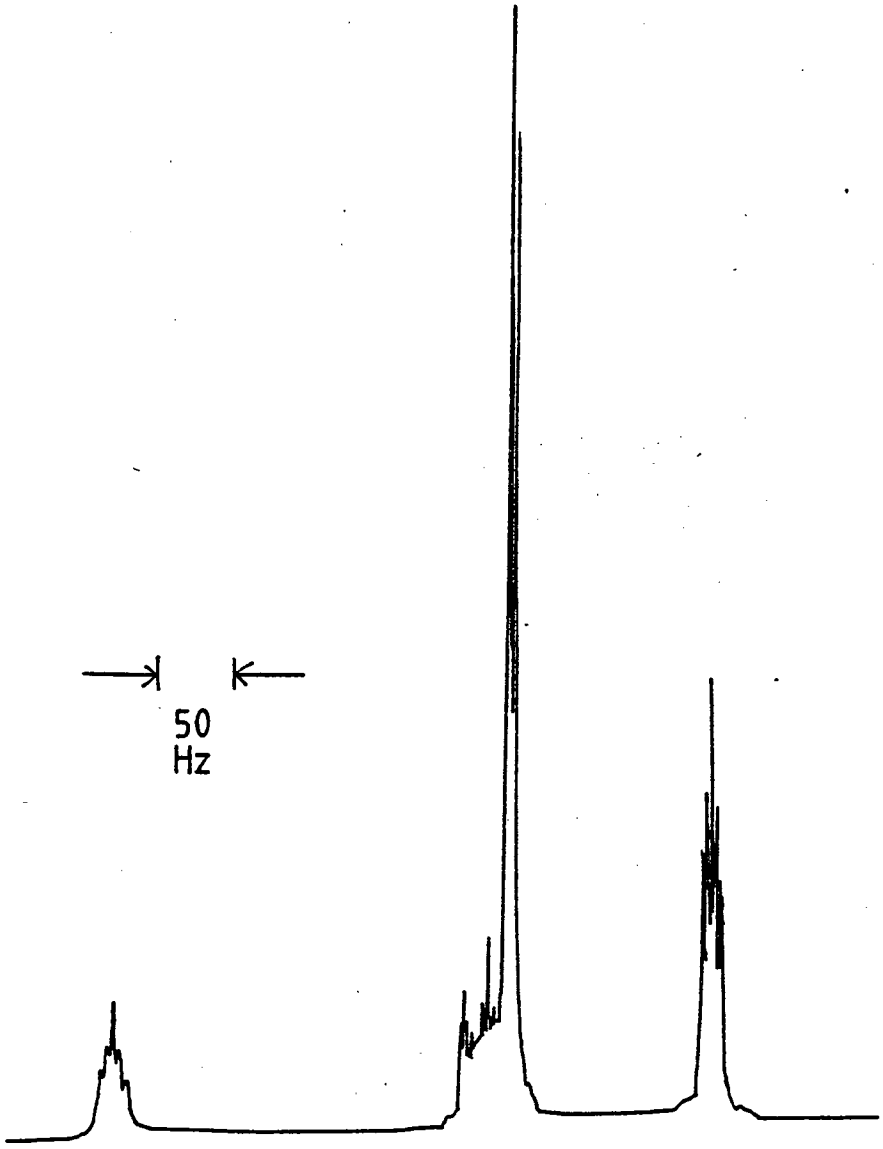


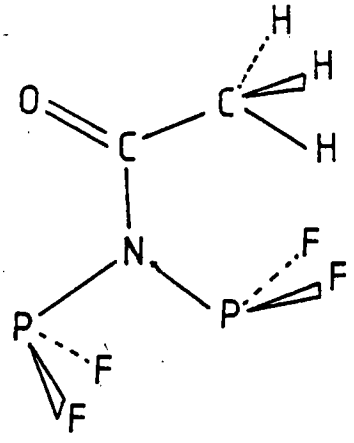
Figure 8:5 The normal $[A(X)_2]_2$ pattern - the ^{19}F n.m.r., ^{1}H decoupled, high frequency half, of $^{15}N(SiH_3)(PF_2)_2$.

Figure 8:6C, which was recently confirmed by an e.d. study[225]. If both groups in VI were rotated, there would be unfavourable F--F interactions. In VII $^4J_{PP'}$ is zero due to the extra intervening bonds keeping the lone pairs far apart, and also reducing the through bond contribution drastically.

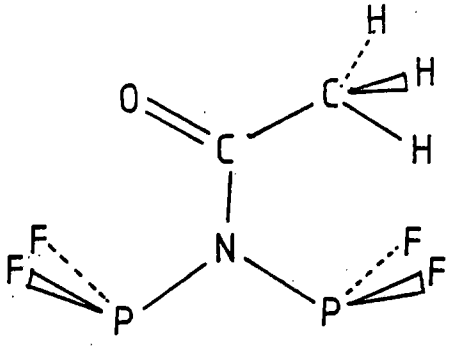
The suggested conformation of VI leads to several predictions. Increasing the temperature will increase the PF_2 group torsions but there will still be no lone pair interactions and so $^2J_{PP'}$ will not vary significantly with temperature, unlike $N(MH_3)(PF_2)_2$ (M = C[121], Si, Ge). But the fluorine-lone pair interactions will change with increased torsions, so $^3J_{PF'}$ (and δF) will vary with temperature, though $^1J_{PF}$ need not be affected. These predictions were soon verified by the variable temperature study, Table 8:3, and the percentage change in $^3J_{PF'}$ is the highest observed for an $N(PF_2)_2$ compound.

Although $^4J_{PH}$ is only 4.5 Hz in VI, this seems rather large, for $^4J_{PH}$ in $PF_2[NH(Bu^t)]$, $PF[NH(Bu^t)]_2$, and cyclodiphosph-IIIazanes is about 0.7 Hz[25,127]. This may be a consequence of the unusual geometry of VI which directs a P lone pair towards the CH_3 group part of the time, which would lead to a larger coupling. The corresponding couplings in VII are too small to be resolved. Not surprisingly for VI and VII, $^5J_{FH}$ is very small, and not resolved, respectively.

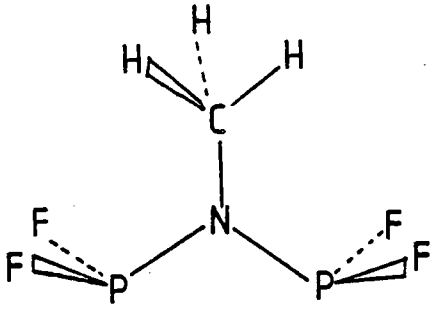
Although the Me_3Si proton resonances of III could not be identified, all the peaks in the Me_3Si region were singlets, implying no couplings to these nuclei.



A



B



C

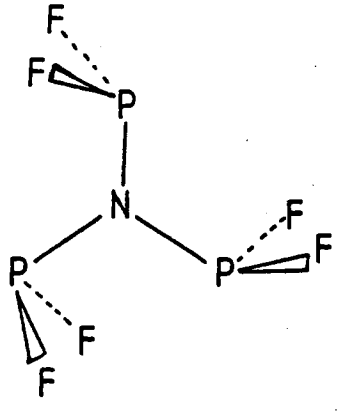


Figure 8:6 Possible conformations of $N[CO(CH_3)](PF_2)_2$, and related species.

Chapter 9

Halogen Exchange Reactions of $PF_2(NMe_2)$

"I understand how, I do not understand why.(Winston Smith)"

"1984", George Orwell.

Introduction

It would be useful to synthesise molecules which on the basis of the possible intramolecular F--H interactions, could be predicted to have only one conformer, such as $NH(PF_2)(PF_4)$. Another such compound might be $PF_2[NH(SiF_3)]$. Though the synthesis of this compound was unsuccessful, it did lead to the discovery of an unexpected exchange process involving the fluorines of $PF_2(NMe_2)$.

Results and Discussion

The reaction of $PF_2(NH_2)$ with SiF_3Cl (Experimental Section 9:1) was expected to proceed according to equation 9:1.

$$3PF_2(NH_2) + 2SiF_3Cl \rightarrow 2PF_2[NH(SiF_3)] + PF_2Cl + NH_4Cl \quad \ldots.9:1$$

Though PF_2Cl was detected along with a white solid, no new PF_2- or SiF_3- amines were observed either by ^{31}P or ^{19}F n.m.r. spectroscopy, even when using $PF_2(^{15}NH_2)$ to aid detection or when

recording spectra without warming the samples above 223 K.

It is unlikely that $PF_2[NH(SiF_3)]$ could have been formed and then completely decomposed without being detected, so an alternative source of PF_2Cl must be sought. Possibly the SiF_3Cl cleaves the P-N bond, to give PF_2Cl and $SiF_3(NH_2)$, and if this was immediately followed by the formation of an adduct between $SiF_3(NH_2)$ and SiF_3Cl, then this would also explain the origin of the white solid. Liquid-phase room temperature reactions of silicon tetrahalides with amines usually[226] lead to the formation of solid adducts, though compounds such as $X_3Si(NR_2)$(X=Cl,F) can also be produced under more controlled conditions[227,228]. An earlier study[229] of this system seemed to indicate the initial formation of an unidentified amine, with two N-H stretches in its i.r. spectrum, (perhaps $SiF_3(NH_2)$?) which rapidly decomposed.

To test the P-N cleavage mechanism reaction 9:2 was attempted as both products are already known[31,230], but no reaction had occurred after 30 minutes at 295 K.

$$PF_2(NMe_2) + SiF_3Cl \rightarrow PF_2Cl + SiF_3(NMe_2) \quad \ldots 9{:}2$$

However after 30 minutes at 333 K the solution had turned green. Comparison of ^1H, ^{19}F, and ^{31}P n.m.r. spectra with literature data[31,73,231, 232] showed that as well as a trace of $PF_2(NMe_2)$, $PF(Cl)(NMe_2)$ and $PCl_2(NMe_2)$ were also present and the SiF_3Cl had been replaced by SiF_4. Obviously an exchange reaction - equation 9:3 - was occurring.

$$SiF_3Cl + PF_2(NMe_2) \rightarrow SiF_4 + PF(Cl)(NMe_2)$$

$$\downarrow \; SiF_3Cl$$

$$\rightarrow PCl_2(NMe_2) + SiF_4 \quad \ldots 9{:}3$$

Unfortunately this reaction neither proves nor invalidates the original hypothesis on the $PF_2(NH_2)$ reaction, and there the matter has to rest. Other exchange reactions of $PF_2(NMe_2)$ were now investigated, however.

It was found that PF_2Cl could also chlorinate $PF_2(NMe_2)$, giving PF_3 as the by-product. However this reaction was slower than equation 9:3, and even after 90 minutes at 350 K was less complete. Mutual electrostatic repulsion of the phosphorus lone pairs as the PF_2Cl approached the amines was probably an important factor in the slower rate observed here.

It proved to be quite difficult to induce an exchange reaction between PF_2Br and $PF_2(NMe_2)$ (Experimental Section 9:4), but after prolonged heating the products were identified as $PF(Br)(NMe_2)$, $PBr_2(NMe_2)$ and PF_3[31,231,233]. The slower rate can again be ascribed to lone pair interactions, though the increased steric hinderance due to the bulky bromine atom may be the overriding factor.

When another worker[234] reacted $PF_2(NCS)$ with $PF_2(NMe_2)$, n.m.r. spectra showed that the expected insertion reaction 9:4 had clearly not occurred.

$$PF_2(NCS) + PF_2(NMe_2) \rightarrow Me_2NC(S)[N(PF_2)_2] \quad \ldots 9{:}4$$

Forearmed with the above exchange reactions, the results were interpreted as being an equivalent pseudo-halogen exchange, with the products being $PF(NCS)(NMe_2)$, $P(NCS)_2(NMe_2)$ and PF_3.

These results are not unique, for it is known[235] that PCl_3 can chlorinate $PF_2(NMe_2)$ to yield $PCl_2(NMe_2)$ and PF_2Cl, although no evidence for the intermediate $PF(Cl)(NMe_2)$ could be found, even when using excess amine, while reaction 9:5 was reported recently[236].

$$2BCl_3 + 3PF_2[N(SiMe_3)_2] \rightarrow 3PCl_2[N(SiMe_3)_2] + 2BF_3 \quad \ldots 9:5$$

Similar exchanges may be responsible for other reactions previously unexplained. For example, although PF_2Br reacts with $PF_2[NH(SiH_3)]$ to give SiH_3Br, no $NH(PF_2)_2$ is formed[47]: instead an orange solid is deposited. Perhaps exchange followed by polymerisation is occurring, equation 9:6.

$$PF_2Br + PF_2[NH(SiH_3)] \rightarrow PF(Br)[NH(SiH_3)] + PF_3$$

$$\downarrow PF_2[NH(SiH_3)]$$

$$\text{polymerisation, cyclisation} \leftarrow PF_2[NH(PF_2[NH(SiH_3)])] + SiH_3Br \quad \ldots 9:6$$

The slow rate of reaction is compatible with the $PF_2Br/PF_2(NMe_2)$ reaction. The reaction between $PF_2[N(SiH_3)_2]$ and PF_2Br (Chapter 4) might also be interpreted in a similar way as here too SiH_3Br was formed but no $N(PF_2)_2(SiH_3)$ was detected. The gas phase[32] preparation of $PF_2(NH_2)$ from $PF_2X(X=Cl,Br)$ and NH_3 gives a >95% yield, while the liquid phase reaction only gives ~25% - halogen exchange and

polymerisation in the more concentrated medium could be responsible for this.

Obviously such exchange reactions warrant serious consideration, both as undesirable side reactions and as preparative methods, for the apparent yields as judged by the n.m.r. spectra were very high. Normally one considers the PF_2 group to be a fairly unreactive entity which may be transferred from molecule to molecule. These show that the fluorines are simply not as non-labile as is generally believed.

Chapter 10

Conclusions and Future Work

"Still crazy, after all these years"

Paul Simon.

A number of new derivatives of $PF_2(NH_2)$ have been synthesised, using NMe_3 as an HX abstractor to overcome the weak basicity of $PF_2(NH_2)$ and some of its derivatives, while Si-N bond cleavage reactions have also proved useful synthetic routes to otherwise unattainable compounds. Some reactions of the new compounds reported with reagents such as HX, S and B_2H_6 were attempted. In most of the compounds reported, F--H interactions are crucial in determining the preferred conformation of the molecule.

During the course of the work the following couplings J_{PX} were found to be large when X was cis to the phosphorus III's lone pair and small when trans to the lone pair:- $^2J_{PNH}$, $^2J(PN^{29}Si)$, $^2J_{PNP}$, $^3J_{PNSiH}$, $^3J_{PNGeH}$, $^3J_{PNPF}$ and $^4J_{PNCCH}$. These couplings were often an average of the two extreme values when spectra were run at ambient temperature, due to fast rotation about the P-N bond, and were best studied by low temperature spectra of "frozen out" conformations. Measuring these couplings in other compounds will show whether a PF_2 or PR_2 group is undergoing fast or restricted rotation about a P-N bond and, if the latter, what its preferred orientation is.

The sharp reduction in $^2J_{PP}$, as first one then two BH_3 groups were complexed with $N(PF_2)_2(SiH_3)$ shows the importance of the lone

pairs with regard to this coupling. A similar effect would be expected if BH_3 complexes of $N(PF_2)_2R$ (R = Me, Et, Ph)[34,97] were examined.

From the number of couplings which were found to depend on the cis/trans orientation of the P lone pair and those which have now been reported in the literature (see Chapter 3) as dependent on the stereochemistry about a P or an N, it seems reasonable to expect that all couplings to a nucleus with a lone pair will be found to vary thus.

Other couplings were also found to vary with the stereochemistry of the molecules - $^2J(FP^{V}{}^{15}N)$ is large when the fluorine can H- bond (and is therefore cis) to an amino proton, (the case is less definitive when a P^{III} intervenes), a Karplus type relationship of $^3J_{FPNH}$ versus $\angle FPNH$ seems to exist, and H- bonding may result in larger values for $^3J(^{29}SiNPF)$ and some J_{FH}'s.

The observation of two N-H stretches and bends in the i.r. spectrum of $PF_2[NH(SiMe_3)]$ showed that, as with[36] $PF_2[NH(SiH_3)]$, two conformations were present due to F--H interactions, and the relative amounts of each conformer were found to vary with temperature. However very little n.m.r. data was collected for this molecule. Labelling it with ^{15}N would make several more coupling constants resolvable, namely $^1J(P^{15}N)$, $^2J_{PH}$, $^2J(P^{29}Si)$, $^3J(P^{13}C)$, $^4J_{PH}$ and $^5J_{FH}$. The orientation of the PF_2 group will obviously be relevant in determining the value of several of these couplings and low temperature n.m.r. might successfully freeze out one of the two conformers, which one being easily determined from the above couplings. Cleavage of the Si-N bond of $PF_2[NH(SiMe_3)]$ might be a useful synthetic route for introducing other groups into the molecule (see the reagents suggested for the

silyl amines later on).

The four germyl amines prepared are much more stable than $N(GeH_3)_3$[45] (although they decompose at room temperature, via elimination of GeH_2) and this is suggested as due to intramolecular F--H interactions between the germyl protons and the fluorines. From the n.m.r. spectra it was deduced that in $PF_2[NH(GeH_3)]$ and $N(GeH_3)(PF_2)_2$ the PF_2 groups were orientated to maximise F--H interactions, while in $PF_2[N(GeH_3)_2]$ fast rotation occurred about the P-N bond (but even this could be between two extreme structures with maximum F--H interactions between first one then the other GeH_3 group and the fluorines). Equivalent structures are proposed for the very much more stable silyl analogs.

Very low temperatures might slow up rotation about the P-N bond in $PF_2[N(MH_3)_2]$ (M = C, Si, Ge) so that it became possible to resolve two different $^3J_{PH}$'s and $^4J_{FH}$'s for each compound, as well as two $^2J_{PM}$'s (M = ^{13}C, ^{29}Si), as predicted from the dependence of these couplings upon the P lone pair stereochemistry. Similarly, useful information on the conformations of $PF_2(PH_2)$[237] and $PF_2[P(MH_3)_2]$ (M = Si, Ge)[47,238] and $PF_2[^{15}NH(BF_2)]$[239] might be obtained from low temperature - n.m.r.

Study of the chemistry of the germyl amines is unlikely to be very productive, although it might be possible to make complexes of them from $PF_2(NH_2)$ or $NH(PF_2)_2$ complexes, assuming these can be made. The silyl amines hold much greater promise of success however. A large variety of $PF_2(NMe_2)$ complexes is known[24,31,132,240,241] and $PF_2[N(SiH_3)_2]$ might be just as versatile, although syntheses involving elevated temperatures would have to be avoided, displacement of ligands such as norbornadiene and cycloheptatriene, or photochemical methods being more suitable.

Recently King has produced a series of papers[130,147,148,149,242,243,244] on $NMe(PF_2)_2$ - transition metal complexes made via some simple synthetic routes. Many have interesting structures as the $NMe(PF_2)_2$ can split to give PF_2 and $PF_2(NMe)$ which can act as individual ligands, the latter sometimes coordinating through both the P and the N, and the $NMe(PF_2)_2$ can act as either a mono- or bidentate ligand. While the explosive nature of any $N(PF_2)_2(SiH_3)$ complex might be a problem, the structural aspects as well as the large number of $N(PF_2)_2(SiH_3)$ (and $NH(PF_2)_2$) complexes which would be accessible make this area worthy of serious consideration.

Many Si-N cleavage reactions are known[43,46], which may also provide a number of novel new compounds; reaction of the Me_3Si- and silyl amines with, for example, BF_3, $AlCl_3$, $GaCl_3$, SiF_4, PCl_3, NOCl, $AsCl_3$, COF_2, SF_4, $BiCl_3$ being merely the tip of the iceberg. Representing these halides as MX or MX_n, typical products would include $PF_2[NH(M)]$, $M[NH(PF_2)]_n$, $PF_2[N(SiH_3)(M)]$, $PF_2N{=}M$ and $NM(PF_2)_2$, all of which hold potential of having coupling constants which would be dependent on the P lone pair orientation.

Finally, the determination of the structures of the silyl amines must not be overlooked. Prior knowledge of the expected orientation of a PF_2 group gained from examination of coupling constants in these and other molecules might simplify e.d. structural determination in the future.

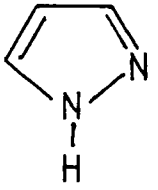
The structure of $NH(PF_2)(PF_4)$ would also be worth confirming though as the P-F bond lengths will all be very similar, perhaps this would best be tackled by an x-ray study at low temperature rather than by e.d.. The formation of a $BH_3.PF_2[NH(PF_4)]$ complex is possible and this would reduce all the couplings which were

abnormally large in the parent compound due to the orientation of the P lone pair (as was observed with the silyl amine-borane complexes) because the lone pair would no longer exist. The molecular structure would probably change, with the PF_2 group rotating about the P-N bond to relieve steric congestion.

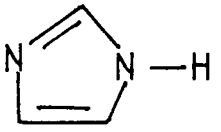
The suggested $HX.PF_2[NH(PF_4)]$ (X = F, Cl, Br) and $PF_5.NH_2(PF_2)$ complexes should be further investigated, and perhaps PF_5 and $NH(PF_2)_2$ should also be reacted. A suitable solvent might enable n.m.r. studies to be made. The reaction of $PF_2[NR(SiH_3)]$ (or $SiMe_3$) (R = H, PF_2) with R_nPF_{5-n} (n = 1-4, R = H, alkyl, aryl, thioalkyl dialkylamino)[169,170,171,172,173] might give more $P^{III}NP^{V}$ compounds and comparison of the coupling constants in such new species with those of $NH(PF_2)(PF_4)$ could be quite informative. A few other compounds which it might be worthwhile to react with PF_5 are $(Me_3Si)_2NP = N(SiMe_3)$[245], and the recently reported[75] $P(CF_3)_2[NH(SiH_3)]$ and $P(CF_3)_2[NMe(SiH_3)]$. If $NH[P'(CF_3)_2](PF_4)$ was synthesised, it too should show three different environments for the P^{V} fluorines, a large $^3J(P'F_b)$, a small $^3J(P'F_a)$ and a small $^2J_{P'H}$ at very low temperatures when a structure similar to that of $NH(PF_2)(PF_4)$ is likely to be assumed by the molecule.

The couplings in $^{15}NH(P'F_2)(PF_4)$ still await the determination of their signs, though it can be deduced that $^3J(P'F_a)$ and $^3J(P'F_b)$ are of opposite signs, and that $^1J(P'^{15}N)$ and $^1J(P^{15}N)$ are positive and negative respectively. The signs of the couplings in $PF_2[^{15}N(GeH_3)_2]$ and $PF_2[^{15}N(SiH_3)_2]$ were found to be the same as for the corresponding couplings[83] in $PF_2[^{15}NH(SiH_3)]$. The magnitude of $^1J(P^{15}N)$ in $H_3B.PF_2[^{15}N(SiH_3)_2]$ suggests that it is positive but this has still to be confirmed experimentally.

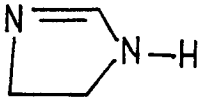
The two pyrrole derivatives are the only examples of PF_2 groups bound to nitrogen atoms in aromatic heterocycles. There is therefore a vast untapped reservoir of potentially interesting compounds awaiting investigation. If time had permitted, the next step would have been the synthesis of PF_2 derivatives of



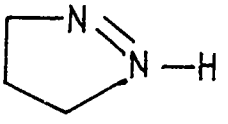
and



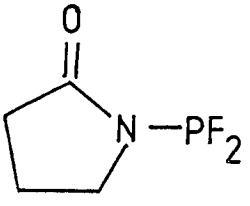
as these compounds might be fluxional, with the PF_2 group moving from nitrogen to nitrogen. Silyl derivatives might also behave similarly. Partially and fully reduced derivatives e.g.



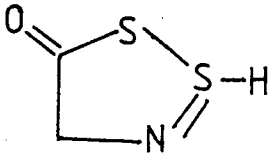
or



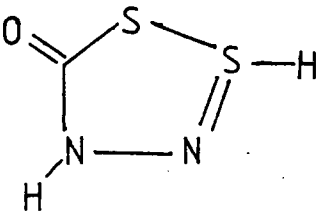
might also prove to be fluxional. One very interesting compound to make would be



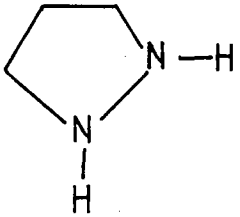
with its obvious relationship to the acetamide derivatives. Perhaps the ultimate in fluxional molecules might be a PF_2 or an SiH_3 compound of



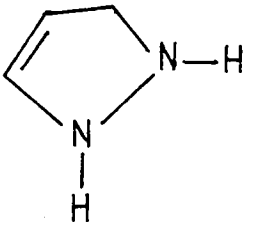
or



In the case of compounds such as



and



substitution of one or two PF_2 groups is possible, and a study of the stereochemical dependence of the various couplings to the phosphorus could be quite rewarding.

A few transition metal complexes of $PF_2(NC_4H_8)$ and $PF_2(NC_5H_{10})$ have been reported[24,31,91,240], and $PF_2(NC_4H_4)$ also might have some future as a ligand. The P-N bond in $PF_2(NC_4H_4)$ was suggested as probably having little $(p\rightarrow d)\pi$ character as the N lone pair is involved in the aromatic π system. Hence the P-N bond may be longer than usual, and a low temperature X-ray study of the crystalline phase would be useful.

Further study of the acetamide derivatives is warranted, the main objective being the isolation of pure samples of the compounds. It has proved possible to make the mono substituted species free of the bis substituted ones[223]. If a pure sample of $N[CO(CH_3)](PF_2)_2$, VI, could be isolated then an X-ray structural determination at low temperatures may confirm the suggested unusual orientation of the PF_2 groups which was deduced from the small value of $^2J_{PP'}$. Other amides should also be investigated to see how widespread is the occurrence of different isomers when $SiMe_3$ derivatives are used, and it is very likely that all other analogs of VI will have a similar structure and hence a small $^2J_{PP'}$. Therefore a combined n.m.r. - X-ray study could be undertaken. Compound VI has some interesting possibilities as a ligand as it may coordinate through either or both of the phosphorus nuclei and even the oxygen as well.

The reactions of $CO[NH(SiMe_3)]_2$ with PF_2Br might lead to $CO[NH(PF_2)]_2$, whose structure - Figure 10:1 - could be interesting as some rotation of the PF_2NH groups is necessary to eliminate lone pair-oxygen interactions. Similarly PF_2Br and $NH(OH)(SiMe_3)$ might give $PF_2[NH(OH)]$ which could also have an interesting structure -

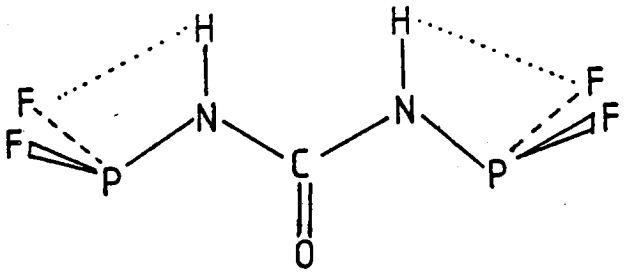


Figure 10:1 A possible structure of $CO[NH(PF_2)]_2$.

Figure 10:2 Possible structures of $NH(OH)(PF_2)$.

Figure 10:2. In both these compounds the coupling constants should be dependent upon the structure adopted. (In $XP[NMe(OMe)]_2$ (X = Cl,Br) hindered rotation about the P-N bonds was observed[246], giving two isomers with different $^3J_{PH}$'s).

As $PF_2H_2(NH_2)$ is extremely unstable, its chemistry is probably not worth investigating. However a vibrational spectroscopy study is not out of the question (especially as the conformation has been predicted from the n.m.r. spectra) though this would best be tackled using solid samples at very low temperatures.

The exchange reactions of $PF_2(NMe_2)$ demonstrate that the PF_2 group need not maintain its identity in all its reactions, is just as susceptible to attack as any other group, and can be a source of undesirable side reactions or a viable preparatory route. (This type of reaction has since been used[236] to prepare $PCl_2[N(SiMe_3)_2]$ and $PCl_2[NBu^t(SiMe_3)]$ from the fluorides and BCl_3).

The $PF_2Br-N_2H_4$ reaction (Appendix 1) barely scratched the surface of this topic. Obviously the product must be positively identified. If it is found to be $PF_2[NH(NH_2)]$ or a further substituted species then labelling it with ^{15}N (at both positions) would provide a whole host of coupling constants which would be dependent on the orientation of the P or N lone pairs. The two isomers $NH_2[N(PF_2)_2]$ and $[NH(PF_2)]_2$ will be easily distinguished: the former will have $^2J_{PP'}$ much larger than $^3J_{PP'}$ of the latter and the ^{31}P spectrum of the former will be a triplet ($^3J_{PH}$) as opposed to the doublet ($^2J_{PH}$) of doublets ($^3J_{PH}$) of the latter.

In conclusion, the original aim of this work - the synthesis of compounds where F--H interactions could be important in determining the structure adopted - has clearly been successful. Other compounds where this might also be true have been suggested

in this chapter, and if synthesised these too would probably generate further research. The variations in certain coupling constants with the molecular geometry has also been noted and it is possible to predict which of several conformations a molecule is likely to adopt, and further work along these lines is likely to be quite productive.

Chapter 11

Experimental Section

"Unnatural deeds do breed unnatural troubles"

W. Shakespeare, Macbeth.

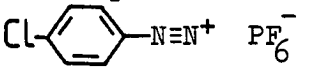
"Many things, base in the doing, please when done"

Ovid, Ars Amatoria.

11:1 Synthetic Methods and Instrumentation

The volatile compounds were handled in standard Pyrex-glass vacuum systems fitted with greased ground-glass taps, or "Sovirel" PTFE greaseless taps when the compounds were grease-soluble (the germyl compounds), when pressures approaching 0.5 atmospheres or greater were anticipated, or for off-line experiments. Apiezon N and L greases were used for taps and joints respectively. All apparatus was dried by filling with SiH_3Br vapour for a few minutes before each experiment. The quantities of the volatile compounds, and some molecular weights, were calculated from gas volumes and pressures, assuming Boyle's Law. Pressures of volatile materials in the vacuum line were measured using a calibrated spiral gauge. The separation of mixtures of volatile compounds was effected by slowly passing the vapours through cold traps held at different, convenient temperatures by slushes formed from suitable solvents and liquid nitrogen or solid carbon dioxide [247]. Commercially available n.m.r. solvents were dried by distilling off flamed-out molecular sieves. Ammonia was stored over sodium then distilled off.

Starting materials for reactions were prepared as described below, and their purity then checked by i.r. or n.m.r. spectroscopy.

Compound	Reagents	Reference
$PCl_2(NMe_2)$	$PCl_3 + HNMe_3$	248
$PF_2(NMe_2)$	$PCl_2(NMe_2) + SbF_3$	248
PF_2X	$PF_2(NMe_2) + HX(X=Cl,Br,I)$	248
$PF_2(NH_2)$	$PF_2X + NH_3$	32, 33
$HN(PF_2)_2$	$PF_2(NH_2) + PF_2X + NMe_3$, then HBr	35
$PF_2[NH(SiH_3)]$	$PF_2(NH_2) + SiH_3Br$	36
SiH_3Br	$PhSiCl_3 + LiAlH_4$, then HBr	249
Me_3SiBr	$HN(SiMe_3)_2 + HBr$	adapted from 43
GeH_4	$KOH, KBH_4, GeO_2, CH_3COOH$	250
GeH_3Cl	$GeH_4 + SnCl_4$	251
GeH_3X	$GeH_3Cl + HX(X=Br,I)$	251
HI	$HI_{(aq)} + P_2O_5$	adapted from 252
HCl	$HCl_{(aq)} + H_2SO_4$	252
PF_5	 + heat	adapted from 253

All other compounds were either commercial products or prepared by standard methods.

Infrared spectra were obtained on a Perkin-Elmer 225 or 557 spectrometer (4000 - 200 cm^{-1}), a Grubb Parsons Spectromajor (8500 - 400 cm^{-1}) or a Beckmann RIIC FS720 interferometer (400 - 50 cm^{-1}) using gas cells fitted with KBr, CsI or polythene windows. The Raman spectra were recorded using Cary 83 or Cary.82 instruments with argon-ion 488-nm laser and 647.1-nm Kr laser excitation respectively. Mass spectra were normally recorded on a double-focussing A.E.I. MS902 spectrometer operating at 70 eV ionising

voltage (1eV ∿ 1.60×10^{-19} J) though lower voltages were sometimes used as well. Dr. S. Cradock assisted in the running (and interpretation) of u.v. photoelectron spectra on a Perkin-Elmer PS16 spectrometer with He(I) (21.22 eV) excitation. Varian Associates XL100, HA100 and, occasionally, EM360 n.m.r. spectrometers were used to obtain ^{1}H, ^{19}F and ^{31}P spectra at 100.0 (60.0 in the case of the EM360), 94.1 and 40.5 MHz respectively. The first two instruments were equipped with variable temperature apparatus and were used for double resonance experiments, the second radio frequency being generated by either a Schlumberger FS30 frequency synthesiser (for the HA100[254]) or the Gyrocode decoupler of the XL100, the frequencies of all the machines being monitored periodically to ensure accuracy. The decoupling frequency could be corrected, after the manner of McFarlane and White[255], to its value in a field such that the ^{1}H resonance of $SiMe_4$ was exactly 100.0 MHz and the chemical shift (δ) then calculated by

$$\delta = \frac{\Xi_c - \Xi_s}{\Xi_s} \times 10^6 \text{ (ppm)}$$

where Ξ_c and Ξ_s were the corrected frequency of the sample, and the standard frequency; δ being positive to high frequency of the standard. The standards used were:-

Compound	Nucleus	Ξ_s (Hz)
$SiMe_3$	^{1}H	100 000 000
CCl_3F	^{19}F	94 093 963
H_3PO_4	^{31}P	40 480 741
$Me_4N^+ I^-$	^{15}N	10 133 352

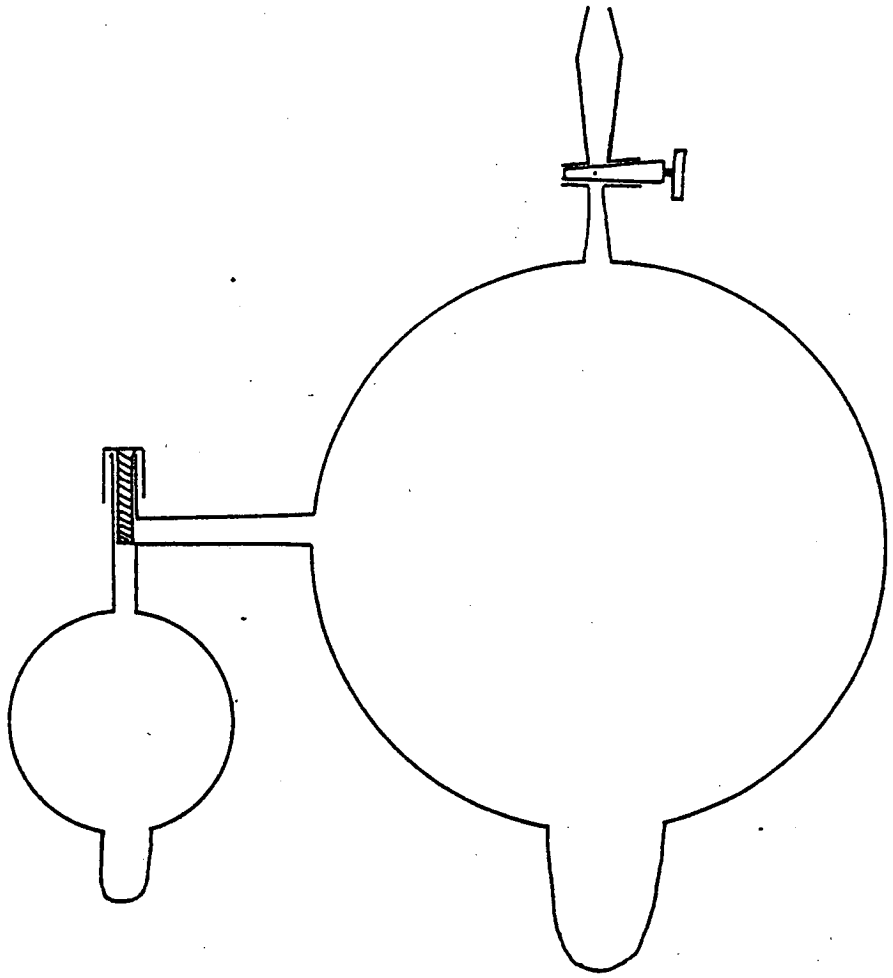


Figure 11:1 The double bulb apparatus used for gas-phase reactions. Relative volumes available: a) 150 ml and 1000 ml, b) 250 ml and 2000 ml.

11.2 Experiments

2:1 Reaction of $PF_2(NH_2)$ with Me_3SiBr

a) No solids formed, indicating no reaction had occurred, even after 10 minutes, when gaseous Me_3SiBr (0.67 mmoles) was injected into $PF_2(NH_2)$ (1.00 mmoles) using a double bulb apparatus of volumes 150 and 1000 mls. Co-condensation at 227 K for 1 hour gave a white solid and fractionation of the volatiles yielded $PF_2[NH(SiMe_3)]$ (<0.1 mmole) retained at 227 K, PF_3 (0.3 mmoles) and traces of Me_3SiBr and $PF_2(NH_2)$ retained at 77 K.

b) Co-condensation of Me_3SiBr (2.0 mmoles) and $PF_2(NH_2)$ (3.0 mmoles) in a 250 ml bulb with alternate warming to 295 K and recondensation at 77 K until no more solids formed (about 4 cycles) yielded $PF_2[NH(SiMe_3)]$ (0.38 mmoles, ca. 20% yield) with $PF_2(NH_2)$ (0.2 mmoles), Me_3SiBr (0.2 mmoles) and a trace of PF_3 also being recovered.

2:2 Reaction between $PF_2(NH_2)$, Me_3SiBr and NMe_3

a) Fifty minutes after injecting Me_3SiBr (3.1 mmoles) into a mixture of $PF_2(NH_2)$ (3.0 mmoles) and NMe_3 (3.0 mmoles) as in 2:1a, an estimated 5% reaction had occurred. Condensation as in 2:1b of this mixture, followed by fractionation, yielded $PF_2[NH(SiMe_3)]$ (0.97 mmoles, 33% yield), PF_3 (0.1 mmoles), $PF_2(NH_2)$ (0.3 mmoles) and Me_3SiF (0.8 mmoles).

b) After Me_3SiBr (1.60 mmoles), $PF_2(NH_2)$ (1.20 mmoles) and NMe_3 (1.20 mmoles) were condensed into a 40 ml ampoule fitted with a Sovirel greaseless tap and mixed rapidly by quickly warming to ∿270 K and recooling at 77 K, the cold ampoule was immersed in a 268 K ice-salt bath for 10 minutes. Fractionation afforded

$PF_2[NH(SiMe_3)]$ (0.73 mmoles, 60% yield), with PF_3 (0.3 mmoles) Me_3SiF (0.4 mmoles) and $PF_2(NH_2)$ (0.2 mmoles) also being recovered. White solids were left in the ampoule.

2:3 Reaction between $N(SiMe_3)_3$ and PF_2X (X = Cl, Br)

Some $N(SiMe_3)_3$ (0.233 g, 1.0 mmoles) was weighed into an ampoule and PF_2X (3.2 mmoles) condensed onto the solid. Ten minutes at 290 K only produced an amine/halide solution from which PF_2X (3.0 mmoles) could be recovered unreacted. Traces of Me_3SiX (ca. 0.15 mmoles) were noted but heating the ampoule to 330 K released no other volatile material.

3:1 Gas-phase reaction between $PF_2(NH_2)$ and GeH_3X (X = Br, I)

No reaction occurred when $PF_2(NH_2)$ (1.00 mmoles) and GeH_3X (0.70 mmoles) were mixed in the gas phase using the double bulb apparatus of Experimental Section 2:1.

3:2 Liquid-phase reaction between $PF_2(NH_2)$ and GeH_3X (X = Br, I)

a) After immersing a 40 ml greaseless tap ampoule containing GeH_3Br (1.00 mmoles) and $PF_2(NH_2)$ (1.50 mmoles) in a salt-ice bath for 5 minutes, traces of solids formed. Fractionation through traps held at 227, 209 and 77 K yielded $PF_2[NH(GeH_3)]$ (0.01 mmoles) from the 209 K trap, and $PF_2(NH_2)$ ($\sim$1.5 mmoles) and GeH_3Br ($\sim$1.0 mmoles) from the 77 K trap.

b) A mixture of GeH_3I (1.00 mmoles) and $PF_2(NH_2)$ (1.50 mmoles) in the 40 ml ampoule was warmed from 77 K to 293 K and recondensed 10 times, traces of solids forming each time. Fractionation yielded GeH_3I ($\sim$1.0 mmoles) in the 227 K trap, $PF_2[NH(GeH_3)]$ (0.02 mmoles), and $PF_2(NH_2)$ ($\sim$1.5 mmoles).

3:3 Reaction between GeH_3X (X = Br, I), $PF_2(NH_2)$ and NMe_3

a) When GeH_3Br (1.10 mmoles), $PF_2(NH_2)$ (1.00 mmoles) and NMe_3 (1.00 mmoles) were warmed to 293 K and recondensed to 77 K three times and fractionated, $PF_2[N(GeH_3)_2]$ (∿0.05 mmoles) was recovered from the 227 K trap; $PF_2[NH(GeH_3)]$ (∿0.1 mmoles)was also recovered, as was $PF_2(NH_2)$ (0.6 mmoles), NMe_3 (0.2 mmoles) and a mixture of GeH_4 and GeH_3F (∿0.1 mmoles in total). Brown, white and yellow solids remained in the ampoule.

b) A mixture of GeH_3I (1.10 mmoles), $PF_2(NH_2)$ (1.00 mmoles) and NMe_3 (1.00 mmoles) was warmed to 293 K for 20 seconds, with brown, white and yellow solids forming rapidly in the liquid. Repeated fractionation yielded $PF_2[N(GeH_3)_2]$ (∿0.1 mmoles), $PF_2[NH(GeH_3)]$ (∿0.25 mmoles), $PF_2(NH_2)$ (0.4 mmoles), and a mixture of GeH_4 and Ge_2H_6 (0.3 mmoles in total).

c) After mixing GeH_3I (2.20 mmoles) and $PF_2(NH_2)$ (1.00 mmoles), three additions of NMe_3 (1.00, 0.50 and 0.70 mmoles) were made, the ampoule being warmed to 290 K for ∿10 seconds after each addition then cooled to 77 K. Fractionation afforded $PF_2[N(GeH_3)_2]$ (0.3 mmoles), $PF_2[NH(GeH_3)]$ (0.15 mmoles), $PF_2(NH_2)$ (0.35 mmoles), NMe_3 (∿0.05 mmoles) and Ge_2H_6 (∿0.05 mmoles).

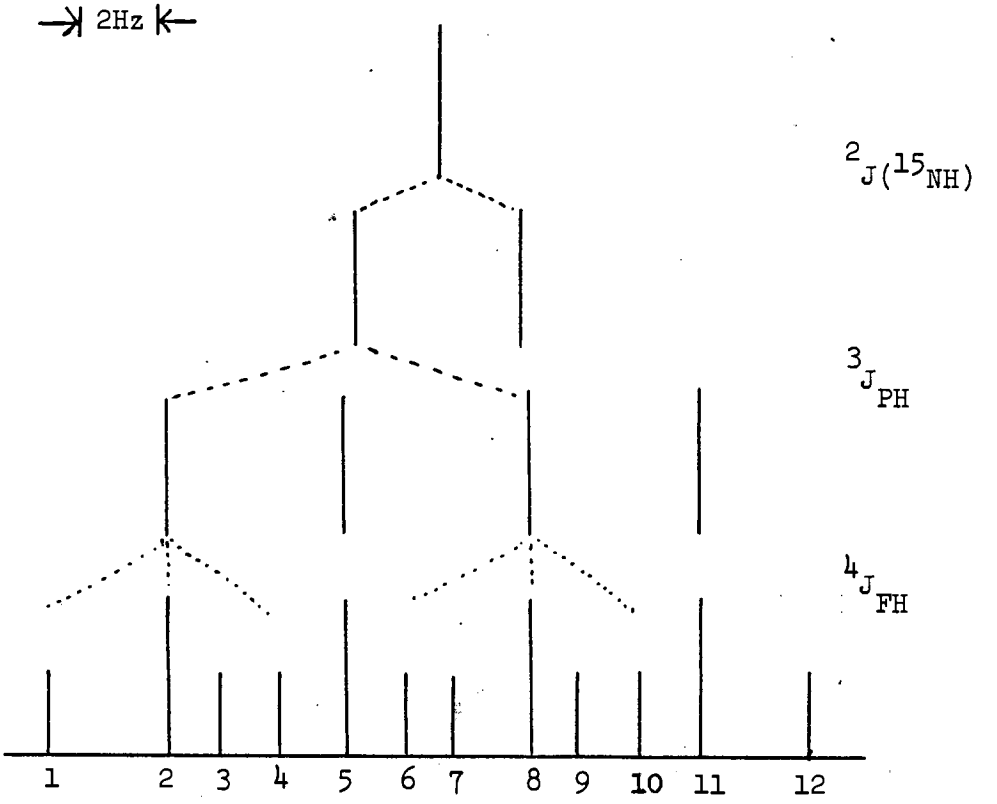
3:4 Synthesis of $N(GeH_3)(PF_2)_2$

There was no reaction between $NH(PF_2)_2$ (1.80 mmoles) and GeH_3I (2.00 mmoles) at 293 K in the liquid or gas phase. When NMe_3 (0.6 and 1.4 mmoles) was added stepwise to the mixture, with warming to 290 K after each addition for ∿15 seconds, multicoloured solids formed rapidly in the liquid. Repeated fractionation through traps at 227, 209 and 77 K eventually yielded GeH_3I (0.3 mmoles) from the 227 K trap, $N(GeH_3)(PF_2)_2$ just stopped at 209 K, and $NH(PF_2)_2$ (0.6 mmoles)

Figure 11:2

N.m.r. double resonance experiments to relate the signs of the various coupling constants of $PF_2[^{15}N(GeH_3)_2]$

Proton n.m.r. spectrum of $PF_2[^{15}N(GeH_3)_2]$



Line	Decoupling Frequency (Hz)	Relative Signs of Couplings (K)
2	40 487 820 ± 5	$(P^{15}N) \gtrless (^{15}NH)$
5	40 487 905 ± 5	
1	40 486 605 ± 10	$(PF) \gtrless (FH)$
1	94 090 960 ± 30	$(FP) \gtrless (PH)$
12	94 092 140 ± 20	
2	10 133 480 ± 10	$(P^{15}N) \gtrless (PH)$
8	10 133 565 ± 5	

Assuming $^1K_{PF}$ is -ve, then $^4K_{FH}$ is +ve, $^3K_{PH}$ is +ve, $^1K(P^{15}N)$ is -ve, $^2K(^{15}NH)$ is +ve.

i.e. $^1J_{PF}$ is -ve, $^4K_{FH}$ is +ve, $^3J_{PH}$ is +ve, $^1J(P^{15}N)$ is +ve, $^2J(^{15}NH)$ is -ve.

NMe_3 (0.1 mmoles) GeH_4 (0.35 mmoles) and a trace of Ge_2H_6, retained at 77 K. The $NH(PF_2)_2$ recovered was then reacted with more GeH_3I (1.00 mmoles) and NMe_3 (0.4, 0.5 mmoles) to yield similar ratios of products. From the amount of GeH_3I recovered, the crude yield of $N(GeH_3)(PF_2)_2$ is estimated at 80%, but after the prolonged fractionation process, only ca. 0.5 mmoles of almost pure sample could be isolated, equivalent to a 28% yield.

3:5 Preparation of $PF_2N(GeH_3)(SiH_3)$

An intimate mixture of $PF_2[NH(SiH_3)]$ (0.4 mmoles) and GeH_3I (0.4 mmoles) failed to react at 293 K. After condensing in NMe_3 (0.4 mmoles) and warming the reactants to 290 K, white and yellow solids formed, and after 15 to 20 seconds reddish brown solids were also present. The volatile materials were immediately condensed into an n.m.r. tube and spectra recorded at 223 K.

4:1 Reaction of $PF_2[NH(SiH_3)]$ with SiH_3Br

No reaction occurred between $PF_2[NH(SiH_3)]$ (1.5 mmoles) and SiH_3Br (1.0 mmoles) after 15 minutes at 293 K in the liquid phase, the starting materials being recovered without loss.

4:2 Preparation of $PF_2[N(SiH_3)_2]$

Initially, NMe_3 (2.4 mmoles) was condensed into a mixture of $PF_2[NH(SiH_3)]$ (2.2 mmoles) and SiH_3Br (2.5 mmoles) in a 40 ml ampoule. Warming to 293 K for about 10 seconds produced white solids, and fractionation yielded 2.0 mmoles of an 85:15 mixture of $PF_2[N(SiH_3)_2]$ and $PF_2[NH(SiH_3)]$, retained at 177 K and SiH_3F and SiH_3Br (0.6 mmoles in total), retained at 77 K. Next, the mixture of amines, 1.0 mmoles at a time was reacted as above with SiH_3Br (0.5 mmoles) and NMe_3 (0.4 mmoles), yielding $PF_2[N(SiH_3)_2]$ (1.7 mmoles, 77% yield based

on $PF_2[NH(SiH_3)]$ taken), volatile at 195 K, involatile at 177 K, and SiH_3F (0.4 mmoles), stopped at 77 K.

4:3 Reaction between $NH(PF_2)_2$ and SiH_3Br

There was no evidence, visual or spectroscopic, of any reaction between $NH(PF_2)_2$ (1.0 mmoles) and SiH_3Br (1.0 mmoles) after 15 minutes at 293 K in the 40 ml ampoule, the reactants being recovered in full.

4:4 Preparation of $N(PF_2)_2(SiH_3)$

The apparatus used was dried more carefully than usual with SiH_3Br for this preparation. Trimethylamine (1.0 mmoles) was condensed onto a mixture of $NH(PF_2)_2$ (0.8 mmoles) and SiH_3Br (1.2 mmoles) in the 40 ml ampoule. Warming the reactants to room temperature resulted initially in the formation of white solids, then some orange-brown solids. After 15 seconds, the volatiles were fractionated yielding $N(PF_2)_2(SiH_3)$ (0.7 mmoles, 87% yield) volatile at 195 K, involatile at 177 K, and a mixture of SiH_3F, SiH_3Br and PF_3 (0.5 mmoles in total), retained at 77 K.

4:5 Reaction of $PF_2[N(SiH_3)_2]$ with HBr

Equimolar quantities of amine and acid were reacted at ambient temperature in an n.m.r. tube. White solids formed instantly, and ^1H and ^{31}P n.m.r. showed the presence of PF_2Br, SiH_3Br, some $HN(SiH_3)_2$ and unreacted amine.

4:6 Reaction of $N(PF_2)_2(SiH_3)$ with HBr

In a similar fashion a 3:1 ratio of acid to amine was reacted with similar results.

4:7 Reactions of $PF_2[N(SiH_3)_2]$ and $N(PF_2)_2(SiH_3)$ with H_2O

The exact quantity of H_2O added was not accurately measured, but small amounts were reacted by either passing the amine through sections of the vacuum line which had previously been in contact with water vapour, and then recording the i.r. spectrum, or recording n.m.r. spectra using $CDCl_3$ which had not been dried before use as the solvent. Products a) $PF_2[N(SiH_3)_2]$:- $PF_2[NH(SiH_3)]$, $PF_2(NH_2)$, PF_3, $O(PF_2)_2$, SiH_4, $O(SiH_3)_2$, SiH_3F; b) $N(PF_2)_2(SiH_3)$:- as above, except $NH(PF_2)_2$ instead of $PF_2[NH(SiH_3)]$.

4:8 Reaction of $PF_2[N(SiH_3)_2]$ with sulphur

Excess sulphur (0.075 g, 0.25 mmoles) was heated with $PF_2[N(SiH_3)_2]$ (0.20 mmoles) in an n.m.r. tube in $CDCl_3$ solution, as described in Table 4:8 but ^1H and ^{31}P n.m.r. spectra showed only the decomposition of the amine to SiH_3F and presumably P-N polymer (undetected), without the formation of any phosphorus V species.

4:9 Reaction of $PF_2[N(SiH_3)_2]$ with PF_2Br

The n.m.r. tube reaction of $PF_2[N(SiH_3)_2]$ (0.25 mmoles) with PF_2Br (0.6 mmoles) was monitored by ^1H and ^{31}P n.m.r. for 24 hours at 293 K. Though SiH_3Br was formed, so was a yellow solid, and the amine decomposed with, apparently, no replacement of SiH_3 groups by PF_2 groups.

4:10 Reaction between $PF_2[N(SiH_3)_2]$ and PF_5

Equimolar quantities of $PF_2[N(SiH_3)_2]$ and PF_5 were reacted in $CDCl_3$ at 290 K for a few minutes in an n.m.r. tube before

recording ^{31}P spectra at 223 K. Apart from hydrolysis products, some $PF_2(NPF_3)$ was detected. Unreacted $PF_2[N(SiH_3)_2]$ and a large quantity of PF_3O were also present.

4:11 N.m.r. tube reaction of $N(PF_2)_2(SiH_3)$ with PF_3O

No reaction occurred between $N(PF_2)_2(SiH_3)$ and PF_3O in $CDCl_3$ after 30 minutes at 293 K. The amine decomposed after 30 minutes at 333 K.

4:12 N.m.r. tube reaction of $N(PF_2)_2(SiH_3)$ with $Mo(CO)_4C_7H_8$

No reaction occurred between equimolar quantities of these reagents in $CDCl_3$ at 223 K. After 30 minutes at 303 K, although no products could be detected, the amount of $N(PF_2)_2(SiH_3)$ was clearly substantially reduced as 10 times as many pulses were now required to get an acceptable ^{31}P spectrum.

4:13 Preparation of $H_3B.PF_2[N(SiH_3)_2]$

Typically, $PF_2[N(SiH_3)_2]$ (0.3 mmoles) and B_2H_6 (0.2 mmoles) were reacted in an n.m.r. tube at 290 K in $CDCl_3$, ^{31}P, ^{19}F and ^{1}H n.m.r. spectra showing $H_3B.PF_2[N(SiH_3)_2]$ as the only product.

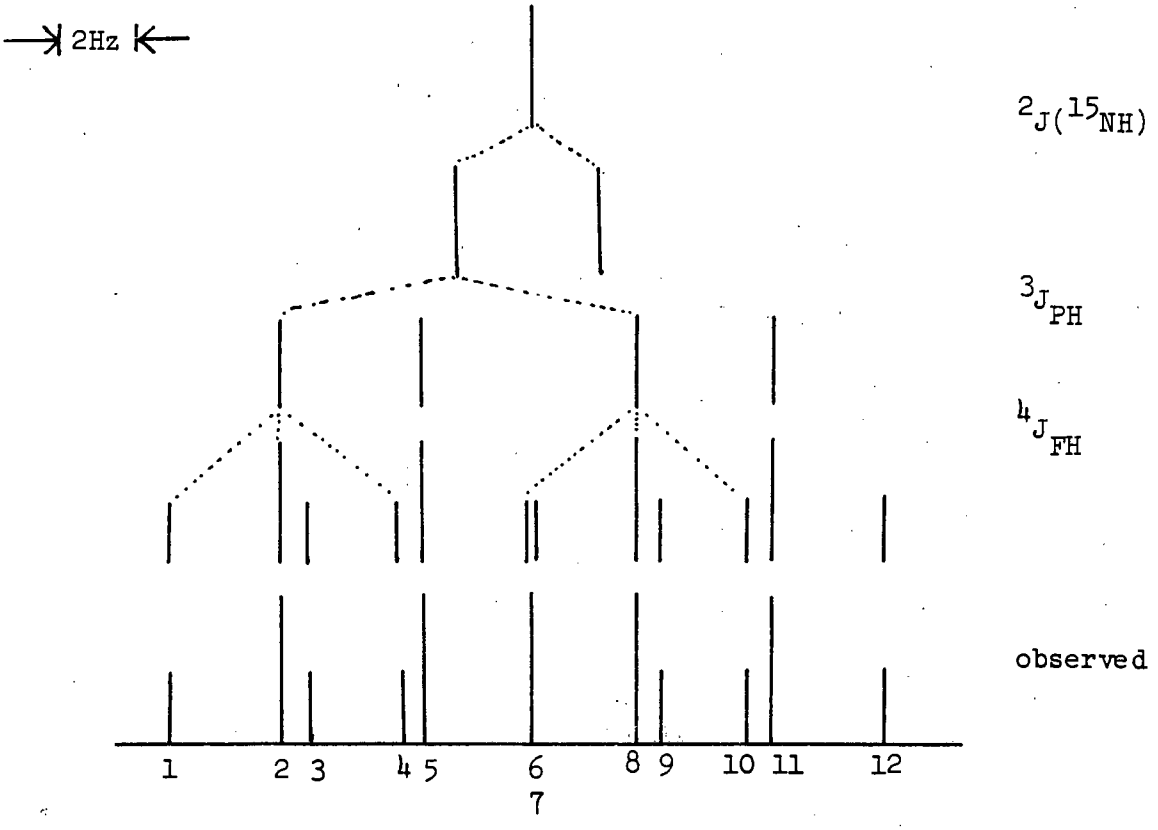
4:14 Reaction between B_2H_6 and $N(PF_2)_2(SiH_3)$

Several molar ratios (1:1, 2:1 and 3:1) of $N(PF_2)_2(SiH_3)$ and B_2H_6 were reacted in n.m.r. tubes, with $CDCl_3$ as solvent, by warming to 290 K for a few moments and then recording spectra at 223 K or, occasionally, at 290 K. Both $H_3B.PF_2[N(PF_2)(SiH_3)]$ and $N[PF_2(BH_3)]_2(SiH_3)$ were detected in every case, the latter always being the final product.

Figure 11:3

N.m.r. double resonance experiments to relate the signs of the various coupling constants of $PF_2[^{15}N(SiH_3)_2]$

Proton n.m.r. spectrum of $PF_2[^{15}N(SiH_3)_2]$



Line	Decoupling Frequency (Hz)	Relative Signs of Couplings (K)
2	40 487 984	$(P^{15}N) \not= (^{15}NH)$
5	40 488 061	
1	40 486 745	$(PF) \not= (FH)$
1	94 090 855	$(F^{15}N) = (^{15}NH)$
3	94 090 844 ± 2	
12	94 092 090 ± 5	$(FP) \not= (PH)$
5	10 133 631 ± 5	$(^{15}NP) \not= (PH)$
8	10 133 709	
10	10 133 706	$(^{15}NF) = (FH)$

Assuming $^1K_{PF}$ is -ve, then $^4K_{FH}$ is +ve, $^2K(^{15}NF)$ is +ve,

$^2K(^{15}NH)$ is +ve, $^1K(P^{15}N)$ is $\pm$ve, $^3K_{PH}$ is +ve

i.e. $^1J_{PF}$ is -ve, $^4J_{FH}$ is +ve, $^2J(F^{15}N)$ is -ve,

$^2J(^{15}NH)$ is -ve, $^1J(P^{15}N)$ is +ve and $^3J_{PH}$ is +ve.

5:1 Synthesis of $NH(PF_2)(PF_4)$

After carefully drying the 40 ml ampoule with SiH_3Br, $PF_2[NH(SiH_3)]$ (1.00 mmoles) and PF_5 (1.10 mmoles) were co-condensed at 77 K, then warmed to room temperature for 15 seconds before fractionating the volatiles through traps at 195, 177 and 77 K. Most of the $NH(PF_2)(PF_4)$ (0.90 mmoles) was found in the 195 K trap, another 0.03 mmoles being recovered from the 177 K trap along with some $PF_2(NPF_3)$ (0.03 mmoles). The 77 K trap contained SiH_3F (1.0 mmoles) and PF_3 ($\sim$0.05 mmoles), while traces of white and green solids were observed in the ampoule. Sometimes PF_3O was detected, formed by reaction with traces of water.

5:2 Reaction of PF_5 with $PF_2(NH_2)$

After co-condensing $PF_2(NH_2)$ (0.3 mmoles) and PF_5 (0.2 mmoles) in a 40 ml ampoule, the reactants were warmed to 290 K. White solids were formed, but i.r. spectroscopy showed the only volatile to be $PF_2(NH_2)$ (0.1 mmoles). No evidence for $NH(PF_2)(PF_4)$ or $PF_2(NPF_3)$ could be found.

5:3 Reaction of $PF_2[NH(SiH_3)]$ with $PF_2X(S)$ (X = F, Cl, I) and PF_3O

In a typical experiment, equimolar quantities of $PF_2[NH(SiH_3)]$ and PF_3S were reacted for 1 minute at 290 K in an n.m.r. tube, with $CDCl_3$:TMS::1:1 as solvent, before recording ^{31}P, ^{19}F and ^{1}H spectra at 223 K. No products could be detected, and after 4 hours at 290 K some decomposition of the amine was evident. Heating the samples to 330 K for 2 hours merely totally decomposed the $PF_2[NH(SiH_3)]$. The solutions were now yellow with traces of

yellow solids due to slight decomposition of the PF_3S, which was still present.

5:4 Reaction of $NH(PF_2)(PF_4)$ with HX (X = Cl, Br)

a) Typically, $NH(PF_2)(PF_4)$ (0.3 mmoles) and HX (0.9 mmoles) were reacted for 10 minutes at 290 K in an n.m.r. tube with C_6D_6 as solvent, before recording ^{31}P and ^{19}F spectra. White solids formed slowly, even after the spectra were recorded. Only traces of PF_2X could be found, and unreacted amine was also noted.

b) The reaction was repeated in an ampoule using 100% excess HBr giving, after 30 minutes, traces of PF_2Br, ~20% unreacted $NH(PF_2)(PF_4)$, HBr, and white solids.

5:5 Reaction between PF_5 and $N(SiMe_3)_3$

a) After weighing $N(SiMe_3)_3$ (0.229 g, 0.98 mmoles) into a 100 ml cold finger, PF_5 (3.0 mmoles) was condensed onto the solid, and left for 10 minutes at 290 K, but all the PF_5 was then recovered upon fractionation. A weight loss of 0.0195 g of amine occurred but this may be due to hydrolysis as the amine appeared to be damp when weighed out.

b) Similarly, $N(SiMe_3)_3$ (0.1825 g, 0.75 mmoles) and PF_5 (3.0 mmoles) were reacted in a 250 ml greaseless tap ampoule at 355 K for 1 hour, with occasional agitation of the now molten amine. Again the PF_5 was recovered completely unreacted.

6:1 N.m.r. tube reaction of PF_2H with NH_3

Typically, $^{15}NH_3$ (0.5 mmoles) was thoroughly mixed with $CDCl_3$ and a trace of TMS before condensing PF_2H (0.5 mmoles) onto

the mixture. The tube was then sealed. On warming to room temperature for less than a minute vast quantities of orange-red solids quickly formed. Spectra were recorded at 215 K, but substantial decomposition of the product, $PF_2H_2(NH_2)$, still occurred on each occasion. The only decomposition product noted was PF_3, though some of this was probably present in the PF_3H used. Repeating the reaction at ca. 270 K produced similar results.

6:2 Liquid phase reaction of PF_2H with NH_3

When PF_2H (0.5 mmoles) and NH_3 (0.5 mmoles) were condensed into an ampoule and then warmed to room temperature, yellow solids were formed which later acquired a tan appearance. After one minute, fractionation of the volatiles through traps at 177 K and 77 K gave only PF_3 (0.3 mmoles) in the 77 K trap. After 10 minutes the original solid had darkened further. Heating these solids for 20 minutes failed to release any further volatile material. Similar solids were noted in the two cold-traps after the initial fractionation.

7:1 Reaction of HNC_4H_4 with PF_2X (X = Br or Cl)

Dried degassed pyrrole (ca. 0.107 g, 1.6 mmoles) was reacted with PF_2X (1.8 mmoles) at room temperature in a 40 ml ampoule. The resulting solution polymerised (X = Cl, in 30 minutes, giving a yellow solid; X = Br, in 5 minutes giving a tan solid) and fractionation of the volatiles led to the recovery of PF_2X (X = Cl, 1.8 mmoles, X = Br, 1.45 mmoles).

7:2 Preparation of $PF_2(NC_4H_4)$

a) Dried degassed pyrrole (0.082 g, 1.2 mmoles) was co-condensed with PF_2Cl (1.4 mmoles) and NMe_3 (1.4 mmoles). On warming to room temperature white solids formed and i.r. spectroscopy showed that the reaction was complete after ca. 30 minutes. Fractionation of the volatiles yielded $PF_2(NC_4H_4)$ (0.7 mmoles, 58% yield) involatile at 209 K, volatile at 227 K. A mixture of PF_3 and PF_2Cl (0.45 mmoles) was recovered from the 77 K trap.

b) Similarly, pyrrole (0.146 g, 2.2 mmoles), PF_2Br (2.3 mmoles) and NMe_3 (2.3 mmoles) were reacted, i.r. spectroscopy showing that reaction was complete within ca. 30 seconds. Fractionation yielded $PF_2(NC_4H_4)$ (1.24 mmoles, 56% yield) and a mixture of PF_3 and PF_2Br (0.60 mmoles).

7:3 Reaction of PF_2Br with $SiH_3(NC_4H_4)$

An excess of PF_2Br (0.3 mmoles) was condensed in an n.m.r. tube with $CDCl_3$ as solvent, and $SiH_3(NC_4H_4)$ (ca. 0.2 mmoles) then added. The tube was warmed to room temperature and the ^1H n.m.r. recorded immediately, showing the presence of $PF_2(NC_4H_4)$, SiH_3Br and a trace of SiH_4. Polymeric material was also recognised from the spectrum and the solution had turned yellow. After 90 minutes, orange floculent solids had been deposited but the ratios of all the products relative to the residual $CHCl_3$ were unchanged.

7:4 Reaction of $PF_2(NC_4H_4)$ with HX (X = Cl, Br)

The room temperature reactions of $PF_2(NC_4H_4)$ (0.35 mmoles) with equimolar quantities of HX were carried out in

n.m.r. tubes, and the ^{1}H n.m.r. spectra of the golden liquids recorded immediately. These, with the ^{31}P spectra, showed that the very rapid reaction produced PF_2X and the usual pyrrole polymer Traces of water lead to some PF_3 and $O(PF_2)_2$ being formed while a trace of unreacted $PF_2(NC_4H_4)$ was noted.

7:5 Reaction of $PF_2(NC_4H_4)$ with sulphur

In an n.m.r. tube with $CDCl_3$ as solvent, sulphur (0.155 g, 0.48 mmoles) and $PF_2(NC_4H_4)$ (0.45 mmoles) were reacted under the following conditions:- 1 day at 290 K then 5 hours at 330 K then 4 days at 290 K then 15 hours at 353 K and another 7 days at 290 K. Monitoring by ^{1}H, ^{19}F and ^{31}P n.m.r. as often as practical showed the gradual decomposition of the heterocycle and formation of PF_3 and the pyrrole polymer, but no P^{V} compounds.

7:6 Formation of $H_3B.PF_2(NC_4H_4)$

Excess diborane (0.4 mmoles) was condensed with $PF_2(NC_4H_4)$ (0.6 mmoles) in an n.m.r. tube with $CDCl_3$ as solvent and reacted at ambient temperature. Yellow solids formed and ^{1}H, ^{19}F and ^{31}P n.m.r. revealed the presence of $H_3B.PF_2(NC_4H_4)$, $H_3B.PF_3$, $H_3B.PF_2H$, excess B_2H_6 and a pyrrole polymer.

8:1 Reaction between $PF_2(NH_2)$ and $CH_3CO.Cl$

When an ampoule into which $PF_2(NH_2)$ (1.50 mmoles) and $CH_3CO.Cl$ (1.00 mmoles) had been co-condensed was warmed to 293 K, white solids, which turned yellow with time, were slowly deposited. After 30 minutes the volatiles were fractionated giving only PF_3 (0.4 mmoles) and an approximately 2:1 mixture (estimated by i.r.) of $CH_3CO.Cl$ and $PF_2(NH_2)$ (0.9 mmoles in total).

8:2 Reaction between $PF_2(NH_2)$, $CH_3CO.Cl$ and NMe_3

When $PF_2(NH_2)$ (1.00 mmoles), $CH_3CO.Cl$ (1.10 mmoles) and NMe_3 (1.00 mmoles) were warmed to 293 K, clouds of white solid formed initially. These settled and then over the next minute a yellowish white solid formed which slowly darkened to an orange-brown. Fractionation yielded an approximately 1:1 mixture of $PF_2(NH_2)$ and $CH_3CO.Cl$ (0.65 mmoles in total).

8:3 Reaction between PF_2Br and $CH_3CO.NH_2$

After being finely ground, acetamide (0.0410 g, 0.8 mmoles) was weighed into an n.m.r. tube and pumped on for 2 days before the addition of $CDCl_3$/TMS//95/5 and then PF_2Br (0.4 mmoles) was condensed in. Warming the reactants to ambient temperature resulted in the formation of white fluffy solids immediately and slowly for the next 30 minutes, by which time traces of $PF_2[NH(CO(CH_3))]$ (as well as unreacted PF_2Br) were detectable by n.m.r..

8:4 Reaction between PF_2Br and bis(trimethylsilyl)acetamide (BSA)

a) After distilling BSA (0.410 g, 2.02 mmoles) and PF_2Br (5.4 mmoles) into a small greaseless tap ampoule, the reactants were shaken at 290 K for 35-40 minutes. The colourless liquid produced was then fractionated through traps at 227, 209 and 77 K. A mixture of PF_3, PF_2Br and $O(PF_2)_2$ (2.65 mmoles in total) was recovered from the coldest trap, while Me_3SiBr (3.1 mmoles) was obtained from the 209 K trap. The contents of the warmest trap were then similarly reacted with further PF_2Br (1.0 mmoles), fractionation yielding only the products involatile at 227 K (and PF_2Br (0.9 mmoles)) which were shown by n.m.r. to be $N[CO(CH_3)](PF_2)_2$ and $CH_3C(NPF_2)(OPF_2)$ and some Me_3SiBr. The vapour pressure of the

mixture was less than 3 mm at 299 K.

b) Similarly, when BSA (0.2000 g, 1 mmole) and PF_2Br (1.0 mmoles) were reacted and fractionated as above, the products from the 227 K trap were shown by n.m.r. to be a mixture of $N(PF_2)(SiMe_3)[CO(CH_3)]$, $O(SiMe_3)(PF_2)$ and the bis-substituted products.

8:5 Reaction between the bis-substituted species and water

When the mixture of products from 8:4 (above) was added to wet $CDCl_3$ in an n.m.r. tube at 290 K, the products were identified as $O(PF_2)_2$, $PF_2[NH(CO(CH_3))]$ and traces of PF_3. Traces of a solid, assumed to be $CH_3CO.NH_2$, were sometimes noted. Alternatively, reacting PF_2Br and BSA in the presence of wet $CDCl_3$ gave the same products.

9:1 Reaction between $PF_2(NH_2)$ and SiF_3Cl

Typically, $PF_2(^{15}NH_2)$ (0.3 mmoles) and SiF_3Cl (0.3 mmoles) were condensed into an n.m.r. tube with $CDCl_3$ as solvent. Only $PF_2(^{15}NH_2)$ was detected when ^{31}P n.m.r. spectra was recorded at 225 K. After warming the tube to 290 K for less than a minute, PF_2Cl was present. Repeating the warming resulted in a white solid being deposited, but ^{19}F n.m.r. spectra showed only $PF_2(^{15}NH_2)$, PF_2Cl and SiF_4 present.

9:2 Reaction of $PF_2(NMe_2)$ with SiF_3Cl

No reaction occurred at 225 K between $PF_2(NMe_2)$ (0.25 mmoles) and SiF_3Cl (0.25 mmoles) in an n.m.r. tube with $CDCl_3$ as solvent. After 40 minutes at 290 K no change was detected and the sample was held at 333 K for 30 minutes, by which time

the solution was green, and ^{1}H, ^{19}F and ^{31}P n.m.r. spectra showed the presence of a trace of $PF_2(NMe_2)$, some $PF(Cl)(NMe_2)$, $PCl_2(NMe_2)$, SiF_4 but no SiF_3Cl.

9:3 Reaction between PF_2Cl and $PF_2(NMe_2)$

Similarly, equimolar quantities of PF_2Cl and $PF_2(NMe_2)$ did not react at 290 K but 90 minutes at 350 K produced $PF(Cl)(NMe_2)$, $PF_2(NMe_2)$, PF_3 and some $PCl_2(NMe_2)$.

9:4 Reaction of PF_2Br with $PF_2(NMe_2)$

Similarly, after prolonged heating, terminating in 8 hours at approximately 365 K, $PFBr(NMe_2)$, $PF_2(NMe_2)$, PF_3 and a little $PBr_2(NMe_2)$ were detected.

A1:1 Reaction of PF_2Br with N_2H_4

Using the double bulb apparatus of Figure 11:1 PF_2Br (1.0 mmole) was injected from the smaller bulb into the larger bulb which contained N_2H_4 (2.0 mmoles) (due to the low vapour pressure of N_2H_4, only about half the hydrazine was in the gaseous state). White clouds formed initially and when these settled after ~10 minutes, the solid was wet and some liquid (N_2H_4?) was present. Fractionation through traps at 240 and 77 K yielded about 0.5 mmoles of a liquid in the former trap and PF_3 and NH_4 (~0.15 mmoles) in the latter. The less volatile liquid was a mixture of some N_2H_4 and what was believed to be $PF_2[NH(NH_2)]$ on the basis of i.r. spectra. Further fractionation of the 240 K sample yielded more NH_3 (0.1 mmole).

Repeating the reaction as above but fractionating after only 3 minutes afforded only PF_3 (0.55 mmoles) and no other products, apart from the white solid.

References

"To punish me for my contempt for authority,

Fate made me an authority myself".

A. Einstein.

1. Alchid Bechil,
"Ordinatio Alchid Bechil Sarcani philosophi", 12th Century ms.

2. J.E. Holmyard,
"The Works of Geber", Dent, London, 1678.
F.S. Taylor,
"The Alchemists", Heinemann, Great Britain, 1952.

3. G.W. von Leibniz,
"Historia inventionis phosphori", Berlin, 1710.

4. C.W. Scheele,
Handl. Svenska Acad., 1771, 32, 120.

5. R.J. Kane,
Phil. Mag., 1847, 36, 105.

6. J.L. Gay Lussac and L.J. Thénard,
Bull. Soc. Philomath., 1808, 1, 302.

7. H. Davy,
Phil. Trans., 1810, 100, 231.

8. J.W. Mellor,
"Treatise on Inorganic and Theoretical Chemistry",
Longmans, London, 1928, Vol. VIII.

9. H. Rose,
Pogg. Ann., 1832, 24, 308; Ann. Chimie, 1834, 11, 131.

10. F. Wöhler and J. von Leibig,
Ann. Chimie, 1834, 11, 139.

11. C.F. Gerhart,
Ann. Chim. Phys., 1846, 18, 188; ibid., 18, 204.

12. A. Michaelis,
Ann. Chimie, 1903, 326, 129.

13. H. Moissan,
Compt. Rend., 1884, 99, 655.

14. H. Moissan,
"Le fluor et ses composés", Paris, 1900.

15. T.E. Thorpe,
Proc. Roy. Soc., 1877, 25, 122.

16. C. Poulenc,
Compt. Rend., 1891, 113, 75; Ann. Chim. Phys., 1891, 24, 584.

17. H.S. Booth and S.G. Frary,
J. Amer. Chem. Soc., 1939, 61, 2927.

18. H.S. Booth and A.R. Bozarth,
J. Amer. Chem. Soc., 1939, 61, 2934.

19. G. Terhaar. M.A. Fleming and R.W. Parry,
J. Amer. Chem. Soc., 1962, 84, 1767.

20. M.A. Fleming,—
Ph.D. Dissertation, Univ. of Michigan, 1963.

21. H. Noth and H.-J. Vetter,
Chem. Ber., 1963, 96, 1298.

22. R.G. Cavell,
J. Chem. Soc., 1964, 1992.

23. D.H. Brown, K.D. Crosbie, G.W. Frazer and D.W.A. Sharp,
J. Chem. Soc. (A), 1969, 551.

24. R. Schmutzler,
Inorg. Chem., 1964, 3, 415.

25. J.S. Harman and D.W.A. Sharp,
J. Chem. Soc. (A), 1970, 1935.

26. I.G. Farbenind. A.-G.,
French Pat. No. 807,769, (1937).

27. H. Moissan,
Bull. Soc. Chim., 1891, 5, 454.

28. R. Schmutzler,
Adv. Fluorine Chem., 1965, 5, 31.

29. T. Kruck,
Angew. Chem. Int. Ed., 1967, 6, 53.

30. M. Fild and R. Schmutzler,
in "Organic Phosphorus Compounds", G.M. Kosolapoff and L. Maier, Wiley Interscience, New York, 1972, Vol. 4.

31. J.F. Nixon,
Adv. Inorg. and Radiochem., 1970, 13, 363.

32. D.W.H. Rankin,
J. Chem. Soc. (A), 1971, 783.

33. J.E. Smith and K. Cohn,
J. Amer. Chem. Soc., 1970, 92, 6185.

34. J.F. Nixon,
J.C.S. Chem. Comm., 1967, 669; J. Chem. Soc. (A), 1968, 2689.

35. D.E.J. Arnold and D.W.H. Rankin,
J.C.S. Dalton, 1975, 889.

36. D.E.J. Arnold, E.A.V. Ebsworth, H.J. Jessop and D.W.H. Rankin,
J.C.S. Dalton, 1972, 1681.

37. J.S. Harmon, M.E. McCartney and D.W.A. Sharp,
J. Chem. Soc. (A), 1971, 1547.

38. J. Persoz,
Ann. Chim. Phys., 1830, 44, 319.

39. A. Stock and K. Somieski,
Ber., 1921, 54, 740.

40. K. Hedberg,
J. Amer. Chem. Soc., 1955, 77, 6491.

41. B. Beagley and A.R. Conrad,
Trans. Faraday Soc., 1970, 66, 2740.

42. D.P. Craig, A. Maccoll, R.S. Nyholm, L.E. Orgel and L.E. Sutton,
J. Chem. Soc., 1954, 332.

43. J.S. Fessenden and R. Fessenden,
Chem. Rev., 1961, 61, 361.

44. E.A.V. Ebsworth,
"Volatile Silicon Compounds", Pergamon, London, 1963.

45. D.W.H. Rankin,
J. Chem. Soc. (A), 1969, 1926.

46. O.J. Scherer,
Organometal. Chem. Rev. A, 1968, 3, 281.

47. D.E.J. Arnold,
Ph.D. Thesis, Edinburgh, 1976.

48. M. Lustig,
Inorg. Chem., 1969, 8, 443.

49. O. Glemser, H.W. Roesky and P.R. Heinze,
Inorg. Nucl. Chem. Letters, 1968, 4, 179;
S. Kongpricha and W.C. Preusse,
Inorg. Chem., 1967, 6, 1915.

50. T.L. Charlton and R.G. Cavell,
Inorg. Chem., 1970, 9, 379.

51. R. Keat,
J. Chem. Soc. (A), 1970, 2732.

52. G.E. Graves, D.W. McKennon and M. Lustig,
Inorg. Chem., 1971, 10, 208.

53. T.L. Charlton and R.G. Cavell,
Inorg. Chem., 1969, 8, 2436.

54. D.D. DesMarteau,
J. Amer. Chem. Soc., 1969, 91, 6211.

55. J.S. Harman, M.E. McCartney and D.W.A. Sharp,
J. Chem. Soc. (A), 1971, 1547.

56. S.M. Hersh,
"Chemical and Biological Warfare", Panther, Great Britain,
1970.

57. F. Bloch, W.W. Hanson and M. Packard,
Phys. Rev., 1946, 69, 127.

58. E.M. Purcell, H.C. Torrey and R.V. Pound,
Phys. Rev., 1946, 69, 37.

59. W.D. Knight,
Phys. Rev., 1949, 76, 1259.

60. W.G. Proctor and F.C. Yu,
Phys. Rev., 1950, 77, 717.

61. W.C. Dickinson,
Phys. Rev., 1950, 77, 736.

62. M.M. Crutchfield, C.H. Dungan, J.H. Letcher, V. Mark and
J.R. van Wazer,
Topics in Phosphorus Chemistry, Vol. 5, 1967.

63. W.G. Proctor and F.C. Yu,
Phys. Rev., 1951, 81, 20.

64. H.S. Gutowsky and D.W. McCall,
Phys. Rev., 1951, 82, 748.

65. M. Karplus,
J. Chem. Phys., 1959, 30, 11; J. Amer. Chem. Soc., 1963,
85, 2870.

66. S. Sternhell,
Quart. Rev., 1969, 23, 236.

67. K. Hirao, H. Nakatsuji and H. Kato,
J. Amer. Chem. Soc., 1973, 95, 31.

68. K.L. Williamson, Y.-F. Li Hsu, F.H. Hall, S. Swager and M.S. Coulter,
J. Amer. Chem. Soc., 1968, 90, 6717.

69. E.G. Finer and R.K. Harris,
Prog. N.M.R. Spect., 1971, 6, 61.

70. R.E. Wasylishen and M. Barfield,
J. Amer. Chem. Soc., 1975, 97, 4545.

71. M. Witanowski and G.A. Webb,
Ann. Reports N.M.R. Spect., 1972 5A, 449, and
references therein.

72. T. Axenrod, P.S. Pregosin and G.W.A. Milne,
Tetra. Letters, 1968, 5293.

73. A.H. Cowley, M.J.S. Dewar, W.R. Jackson and W.B. Jennings,
J. Amer. Chem. Soc., 1970, 92, 1085.

74. T. Kruck, G. Mäueler and G. Schmidgen,
Chem. Ber., 1974, 107, 2421.

75. R.H. Neilson, R. Chung-Yi Lee, and A.H. Cowley,
Inorg. Chem., 1977, 16, 1455.

76. J. Goubeau and J. Jimēnez,
Z. Anorg. Allge. Chemie., 1959, 303, 217.

77. H. Kriegsmann,
Zeit Electrochemie, 1957, 61, 1088.

78. C.C. Cerato, J.L. Lauer and H.C. Beachell,
J. Chem. Phys., 1954, 22, 1.

79. G.S. Laurenson and D.W.H. Rankin,
J. Mol. Structure, 1979, 54, 111.

80. R.A. Jones and A.G. Moritz,
Spectrochim. Acta, 1965, 21, 295.

81. R.A. Nyquist,
Spectrochim. Acta, 1963, 19, 713.

82. A.J. Carty and S.E. Jacobsen,
J.C.S. Chem. Comm., 1975, 175.

83. D.W.W. Anderson, J.E. Bentham and D.W.H. Rankin,
J.C.S. Dalton, 1973, 1215.

84. S. Cradock and D.W.H. Rankin,
J.C.S. Faraday II, 1972, 68, 940.

85. J.G.A. Luijten, F. Rijkens and G.J.M. Van Der Kerk,
Adv. Organometallic Chem., 1965, 3, 397;
F. Glockling,
"The Chemistry of Germanium", Academic Press, London, 1969.

86. E. Hedberg, L. Hedberg and K. Hedberg,
J. Amer. Chem. Soc., 1974, 96, 4417.

87. M. Barrow, E.A.V. Ebsworth, M.M. Harding and S.G.D. Henderson, J.C.S. Dalton, at press.

88. S. Cradock and E.A.V. Ebsworth, J. Chem. Soc. (A), 1967, 1224.

89. E.A.V. Ebsworth, D.W.H. Rankin and G.M. Sheldrick, J. Chem. Soc. (A), 1968, 2828.

90. M.A. Fleming, R.J. Wyma and R.C. Taylor, Spectrochim. Acta, 1965, 21, 1189.

91. C.G. Barlow, R. Jefferson and J.F. Nixon, J. Chem. Soc. (A), 1968, 2692.

92. B.J. Aylett and M.J. Hakim, J. Chem. Soc. (A), 1968, 639.

93. R.M. Lynden-Bell, Trans. Faraday Soc., 1961, 57, 888.

94. R.M. Lynden-Bell, Molecular Physics, 1963, 6, 601.

95. R.K. Harris and R. Ditchfield, Spectrochim. Acta, 1968, 24A, 2089.

96. R.K. Harris, J.R. Woplin, R.E. Dunmur, M. Murray and R. Schmutzler, Ber. Bunsenges. Phys. Chem., 1972, 76, 44.

97. J.F. Nixon, J. Chem. Soc.(A), 1969, 1087.

98. T. Axenrod, P.S. Pregosin and G.W.A. Milne, Chem. Comm., 1968, 702.

99. J.P. Kintzinger and J.M. Lehn, Chem. Comm., 1967, 660.

100. T. Axenrod, M.J. Wieder and G.W.A. Milne, Tetra. Letters, 1969, 401.

101. T. Axenrod, M.J. Wieder and G.W.A. Milne, Tetra. Letters, 1969, 1397.

102. D. Crepaux and J.M. Lehn, Mol. Phys., 1968, 14, 547.

103. D. Crepaux, J.M. Lehn and R.R. Dean, Mol. Phys., 1969, 16, 225.

104. R.M. Lequan and M.P. Simonnin, Tetrahedron, 1973, 29, 3362.

105. M.P. Simonnin, R.M. Lequan and F.W. Wehrli, Chem. Comm., 1972, 1204.

106. J.P. Albrand, D. Gagnaire, J. Martin and J.B. Roberts, Bull. Soc. chim. France, 1969, 40.

107. D. Gagnaire, J.-B. Robert, J. Verrier and R. Wolf, Bull. Soc. chim. France, 1966, 3719.

108. D. Gagnaire and J.-B. Roberts, Bull. Soc. chim. France, 1967, 2240.

109. G. Bulloch, R. Keat and D.S. Rycroft, J.C.S. Dalton, 1978, 764.

110. J. Burdon, J.C. Hotchkiss and W.B. Jennings, Tetra. Letters, 1973, 4919.

111. J.A. Pople and D.P. Santry, Mol. Phys., 1964, 8, 1.

112. R.R. Dean and W. McFarlane, Chem. Comm., 1967, 840.

113. W. McFarlane, Quart. Rev., 1969, 23, 187.

114. C.J. Jameson, J. Amer. Chem. Soc., 1969, 91, 6232.

115. C.J. Jameson and H.S. Gutowsky, J. Chem. Phys., 1969, 51, 2790.

116. W. McFarlane and B. Wrackmeyer, Inorg. Nucl. Chem. Letters, 1975, 11, 719 and references therein.

117. J.R. Schweiger, A.H. Cowley, E.H. Cohen, P.A. Kroon and S.L. Manatt, J. Amer. Chem. Soc., 1974, 96, 7122 and references therein.

118. W. McFarlane and B. Wrackmeyer, J.C.S. Dalton, 1976, 2351, and references therein.

119. G.A. Gray and T.A. Albright, J. Amer. Chem. Soc., 1976, 98, 3857.

120. G.A. Gray and T.A. Albright, J. Amer. Chem. Soc., 1977, 99, 3243.

121. R.W. Rudolph and R.A. Newmark, J. Amer. Chem. Soc., 1970, 92, 1195.

122. D.E.J. Arnold, J.S. Dryburgh, E.A.V. Ebsworth and D.W.H. Rankin, J.C.S. Dalton, 1972, 2518.

123. R.W. Rudolph, R.C. Taylor and R.W. Parry, J. Amer. Chem. Soc., 1966, 88, 3729.

124. D.W.H. Rankin, Personal communication.

125. R.J. Cross, T.H. Green and R. Keat,
J.C.S. Dalton, 1976, 1424.

126. D.E.J. Arnold, E.R. Cromie and D.W.H. Rankin,
Unpublished results.

127. R. Keat and D.G. Thompson,
J.C.S. Dalton, 1978, 634.

128. R. Jefferson, R. Keat, J.F. Nixon, T.M. Painter and L. Stobbs,
J.C.S. Dalton, 1973, 1414.

129. J.F. Nixon and B. Wilkins,
Z. Naturforsch, 1970, B25, 649.

130. R.B. King and J. Gimeno,
Inorg. Chem., 1978, 17, 2396.

131. C.G. Barlow, J.F. Nixon and J.R. Swain,
J. Chem. Soc. (A), 1969, 1082.

132. J.F. Nixon and M.D. Sexton,
J. Chem. Soc. (A), 1969, 1089.

133. J.F. Nixon and A. Pidcock,
Ann. Rev. N.M.R. Spectroscopy, 1969, 2, 345.

134. D.E.J. Arnold and D.W.H. Rankin,
J. Fluorine Chem., 1973, 2, 405.

135. K.W. Muir,
J.C.S. Dalton, 1975, 259.

136. D.G. Thompson,
Personnal communication.

137. W. Mahler,
J. Amer. Chem. Soc., 1964, 86, 2306.

138. S. Cradock, E.A.V. Ebsworth, W.J. Savage and R.A. Whiteford,
J.C.S. Faraday II, 1972, 68, 934.

139. S. Cradock and R.A. Whiteford,
Trans. Faraday Soc., 1971, 67, 3425.

140. S. Cradock and R.A. Whiteford,
J.C.S. Faraday II, 1972, 68, 281.

141. S. Cradock, E.A.V. Ebsworth and J.D. Murdoch,
J.C.S. Faraday II, 1972, 68, 86.

142. E.H. Amonoo-Neizer, R.A. Shaw, D.O. Skovlin and B.C. Smith,
J. Chem. Soc., 1965, 2997.

143. J.G. Wright,
Unpublished results.

144. S. Cradock,
Personal communication.

145. R.C. Dobbie, L.F. Doty and R.G. Cavell,
J. Amer. Chem. Soc., 1968, 90, 2015.

146. G.V. Roeschenthaler, R. Schmutzler and E. Niecke,
Z. Naturforsch. B., 1974, 29, 436.

147. R.B. King and J. Gimeno,
Inorg. Chem., 1978, 17, 2390; ibid, 1978, 17, 2396.

148. R.B. King, J. Gimeno and T.J. Lotz,
Inorg. Chem., 1978, 17, 2401.

149. M.G. Newton, R.B. King, M. Chang and J. Gimeno,
J. Amer. Chem. Soc., 1977, 99, 2802.

150. A.B. Burg,
J. Chem. Educ., 1960, 37, 482.

151. S. Ahrland, J. Chatt and N.R. Davis,
Quart. Rev. Chem. Soc., 1958, 12, 265.

152. A.H. Cowley and M.C. Damasco,
J. Amer. Chem. Soc., 1971, 93, 6815.

153. E.L. Lines and L.F. Centofanti,
Inorg. Chem., 1974, 13, 2796.

154. R.W. Rudolph and C.W. Schultz,
J. Amer. Chem. Soc., 1971, 93, 6821.

155. R. Foester and K. Cohn,
Inorg. Chem., 1972, 11, 2590.

156. K.W. Morse and R.W. Parry,
J. Amer. Chem. Soc., 1966, 88, 3729.

157. L.F. Centofanti and R.W. Parry,
Inorg. Chem., 1968, 7, 1005.

158. G.N. Bockermann and R.W. Parry,
J. Fluorine Chem., 1976, 7, 1.

159. D.E.J. Arnold, E.R. Cromie and D.W.H. Rankin,
J.C.S. Dalton, 1977, 1999.

160. A. Burt and D.W.H. Rankin,
Unpublished results.

161. S. Johnson,
Ph.D. Thesis, Purdue University, 1953.

162. M. Lustig and H.W. Roesky,
Inorg. Chem., 1970, 9, 1289.

163. R. Rogowski and K. Cohn,
Inorg. Chem., 1968, 7, 2193.

164. H.S. Gutowsky, D.W. McCall and C.P. Slichter,
J. Chem. Phys., 1953, 21, 279.

165. R.S. Berry,
J. Chem. Phys., 1960, 32, 932.

166. E.L. Muetterties, W. Mahler and R. Schmutzler,
Inorg. Chem., 1963, 2, 613.

167. E.L. Muetterties, W. Mahler, K.J. Packer and R. Schmutzler,
Inorg. Chem., 1964, 3, 1296.

168. J. Nixon and R. Schmutzler,
Spectrochim. Acta, 1964, 20, 1835.

169. R. Schmutzler,
Angew. Chem. Int. Ed., 1965, 4, 496.

170. D.E.J. Arnold and D.W.H. Rankin,
J.C.S. Dalton, 1976, 1130.

171. J.S. Harman and D.W.A. Sharp,
Inorg. Chem., 1971, 10, 1538.

172. E.L. Muetterties, R. Meakin and R. Hoffman,
J. Amer. Chem. Soc., 1972, 94, 5674.

173. S.C. Peake and R. Schmutzler,
J. Chem. Soc. (A), 1970, 1049.

174. G. Binsch, J.B. Lambert, B.W. Roberts and J.D. Roberts,
J. Amer. Chem. Soc., 1964, 86, 5564.

175. A.H. Cowley and J.R. Schweiger,
J.C.S. Chem. Comm., 1972, 560.

176. G.J. Jordon and D.-L.R. Crist,
Org. Mag. Reson., 1977, 9, 322.

177. R. Goodrich-Haines and J.W. Gilje,
Inorg. Chem., 1976, 15, 470.

178. R. Schmutzler,
in "Halogen Chemistry", Academic Press, London,
1967, Vol. 2, p. 31.

179. G. Milne,
B.Sc. Thesis, Edinburgh, 1975.

180. L.H. Marcus and C.H. Van Dyke,
Inorg. Chem., 1975, 14, 3124.

181. G.I. Drozd, S.Z. Ivin, V.V. Sheluchenko and M.A. Landau,
Zh. Obshch. Khim., 1968, 38, 1653.

182. G.I. Drozd, S.Z. Ivin, V.V. Sheluchenko, B.I. Tetel'baum,
G.M. Luganskii and A.D. Varshavskii,
Zh. Obshch. Khim., 1967, 37, 1631.

183. G.I. Drozd, S.Z. Ivin, V.V. Sheluchenko and B.I. Tetel'baum,
Zh. Obshch. Khim., 1967, 37, 957.

184. G.I. Brozd, S.Z. Ivin and V.V. Sheluchenko,
Zh. Vses. Khim. Obshchestra im. D.I. Mendeleeva,
1967, 12, 472.

185. R.G. Cavell, D.D. Poulin, K.I. The and A.J. Tomlinson,
J.C.S. Chem. Comm., 1974, 19.

186. P.M. Treichel, R.A. Goodrich and S.B. Pierce,
J. Amer. Chem. Soc., 1967, 89, 2017.

187. V.F. Seel and K. Velleman,
Z. Anorg. Allg. Chem., 1971, 385, 123.

188. L.F. Centofanti and R.W. Parry,
Inorg. Chem., 1973, 12, 1456.

189. A. Strich and A. Veillard,
J. Amer. Chem. Soc., 1973, 95, 5574.

190. A.H. Cowley and R.W. Braun,
Inorg. Chem., 1973, 12, 491.

191. J.W. Gilje, R.W. Braun and A.H. Cowley,
J.C.S. Chem. Comm., 1974, 15.

192. C.H. Dungan and J.R. Van Wazer,
"Compilation of Reported ^{19}F N.M.R. Chemical Shifts",
Wiley Interscience, New York, 1970, and references
therein.

193. A.H. Cowley and J.R. Schweiger,
J.C.S. Chem. Comm., 1970, 1492.

194. H.W. Schiller and R.W. Rudolph,
Inorg. Chem., 1971, 10, 2500.

195. R.B. Johannesen,
J. Chem. Phys., 1967, 47, 3088.

196. J. Grosse and R. Schmutzler,
Phosphorus, 1974, 4, 49.

197. R.A. Goodrich and P.M. Treichel,
Inorg. Chem., 1968, 7, 694.

198. J.W. Emsley, J. Feeney and L.H. Sutcliffe,
"High Resolution Nuclear Magnetic Resonance
Spectroscopy", Pergamon Press, Oxford, 1965.

199. C.G. Barlow and J.F. Nixon,
J. Chem. Soc. (A), 1966, 228.

200. T. Kruck and A. Prasch,
Z. Naturforsch, 1964, 19b, 670.

201. F. Mathis,
Phos. and Sulphur, 1976, 1, 109.

202. R.M. Acheson,
"An Introduction to the Chemistry of Heterocyclic Compounds". Wiley Interscience, New York, 1967, and references therein.

203. G.F. Smith,
Adv. Heterocyclic Chem., 1963, 2, 287.

204. M.J.C. Hewson, R. Schmutzler and W.S. Sheldrick,
J.C.S. Chem. Comm., 1973, 190.
W.S. Sheldrick,
J.C.S. Dalton, 1973, 2301.

205. C. Glidewell and D.W.H. Rankin,
J. Chem. Soc. (A), 1970, 279.

206. C. Glidewell, A.G. Robiette and G.M. Sheldrick,
J. Mol. Structure, 1971, 9, 476.

207. S. Cradock,
Unpublished results.

208. W.S. Bhacca, L.F. Johnson and J.N. Shoolery,
"N.M.R. Spectra Catalogue", No. 55,
Varian Assoc., Palo Alto.

209. R.J. Abraham,
"The Analysis of High Resolution N.M.R. Spectra",
Elsevier, Amsterdam, 1971.

210. D.M. Grant, R.C. Hirst and H.S. Gutowsky,
J. Chem. Phys., 1963, 38, 470.

211. R.C. Lord and F.A. Miller,
J. Chem. Phys., 1942, 10, 328.

212. A.R. Katritzky,
Quart. Rev., 1959, 13, 353.

213. P.J. Derrick, L. Asbrink, O. Edqvist, B.O. Jonsonn and E. Lindholm,
Int. J. Mass Spectros. Ion Phys., 1971, 6, 191.

214. J.F. Klebe, H. Finkbeiner and D.M. White,
J. Amer. Chem. Soc., 1966, 88, 3390.

215. H.W. Roesky, B.H. Kuhtz and L.F. Grimm,
Z. Anorg. Allg. Chem., 1972, 389, 167.

216. J.F. Klebe,
Acc. Chem. Res. 1970, 3, 299.

217. C.H. Yoder and D. Bonelli,
Inorg. Nuclear Chem. Letters, 1972, 8, 1027.

218. J. Pump and E.G. Rochow,
Chem. Ber., 1964, 97, 627.

219. C. Kruger, E.G. Rochow and U. Wannagat,
Chem. Ber., 1963, 96, 2138.

220. L. Birkofer and A. Ritter,
Angew. Chem. Int. Ed., 1965, 4, 417.

221. H. Jancke, G. Engelhardt, S. Wagner, W. Dirnens,
G. Herzog, E. Thieme and K. Ruhlmann,
J. Organometallic Chem., 1977, 134, 21.

222. P.K. Hodgson, R. Katz, and G. Zon,
J. Organometallic Chem., 1976, 117, C63.

223. E.A.V. Ebsworth, D.W.H. Rankin, W. Steger and J.G. Wright,
to be published.

224. R.G. Cavell, R.D. Leary, A.R. Sanger and A.J. Tomlinson,
Inorg. Chem., 1973, 12, 1374.

225. D.E.J. Arnold, D.W.H. Rankin, M.R. Todd and R. Seip,
J.C.S. Dalton, 1979, 1290.

226. A.P. Hagen and B.W. Calloway,
J. Inorg. Nucl. Chem., 1972, 34, 487.

227. J.E. Drake and N.P.C. Westwood,
J. Chem. Soc. (A), 1971, 3617.

228. M. Allan, B.J. Aylett, I.A. Ellis and C.J. Porritt,
J.C.S. Dalton, 1973, 2675.

229. D.E.J. Arnold and D.W.H. Rankin,
Unpublished results.

230. J.J. Moscony and A.G. MacDiarmid,
Chem. Comm., 1965, 307.

231. R.G. Montemayor and R.W. Parry,
Inorg. Chem., 1973, 12, 2482.

232. R.B. Johannsen, F.E. Brinckmann and T.D. Coyle,
J. Phys. Chem., 1968, 72, 660.

233. P.G. Maslov,
J. Phys. Chem., 1968, 72, 1414.

234. M.C. McConnell,
B.Sc. thesis, 1976, Edinburgh.

235. Zh. M. Ivanova,
Zh. Obsch. Khim., 1965, 35, 164.

236. R.H. Neilson and A.H. Cowley,
Inorg. Chem., 1975, 14, 2019.

237. R.W. Rudolph and H.W. Schiller,
J. Amer. Chem. Soc., 1968, 90, 3581.

238. D. Hutchinson,
Private communication.

239. D.E.J. Arnold, E.A.V. Ebsworth and D.W.H. Rankin, J.C.S. Dalton, 1976, 823.

240. J.F. Nixon and M.D. Sexton, Chem. Comm., 1969, 827.
J.F. Nixon, J. Chem. Soc. (A), 1967, 1136.

241. R. Schmutzler, J. Chem. Soc., 1965, 5630.
K. Cohn and R.W. Parry, Inorg. Chem., 1968, 7, 46.

242. R.B. King, M.G. Newton, M. Chang and J. Gimeno, Inorg. Chem. Acta 1977, 23, L35; J. Amer. Chem. Soc., 1978, 100, 326; ibid., 100, 1978.

243. M. Chang, R.B. King and M.G. Newton, J. Amer. Chem. Soc., 1978, 100, 998.
R.B. King and J.G. Gimeno, J.C.S. Chem. Comm., 1977, 142.
R.B. King and K-N Chen, Inorg. Chem. Acta, 1977, 23, L19.

244. M.G. Newton, R.B. King, M. Chang, N.S. Pantaleo and J. Gimeno, J.C.S. Chem. Comm., 1977, 531.
M.V. Andreocci, C. Cauletti, C. Furlani and R.B. King, Inorg. Chem., 1979, 18, 954.

245. E. Niecke and W. Flick, Angew. Chem. Int. Ed., 1973, 12, 585.

246. A. Hung and J.W. Gilje, J.C.S. Chem. Comm., 1972, 662.

247. G. Braur, "Handbook of Preparative Inorganic Chemistry", Academic Press, London, 1963 and 1965, Vols. I and II, and references therein.

248. J.G. Morse, K. Cohn, R.W. Rudolph and R.W. Parry, Inorg. Synthesis, 1967, 10, 147.

249. G. Fritz and D. Kummer, Z. Anorg. Chem., 1961, 308, 165.

250. W.L. Jolly and J.E. Drake, Inorg. Synthesis, 1963, 7, 36.

251. S. Cradock, Inorg. Synthesis, 1974, 15, 161.
L.M. Dennis and P.R. Judy, J. Amer. Chem. Soc., 1929, 51, 2321.

252. R.N. Maxson, Inorg. Synthesis, 1939, 1, 147.

253. K.G. Rutherford, W. Redmond and J. Rigamonti, J. Org. Chem., 1963, 26, 5149.

254. A. Charles and W. McFarlane,
Mol. Phys., 1968, 14, 299.

255. W. McFarlane and R.F.M. White,
"Techniques of High Resolution N.M.R.",
Butterworths, London, 1972.

256. A.E. Goya, M.D. Rosario and J.W. Gilje,
Inorg. Chem., 1969, 8, 725.

257. C.J. Pouchert,
"Aldrich Library of Infrared Spectra", 1970,
558G-563H, Aldrich Chem. Co. Inc. New York.

Appendix 1

Hydrazine Derivatives

"It is a capital mistake to theorize before one has data. (Sherlock Holmes)"
"The Adventures of Sherlock Holmes' Scandal in Bohemia", Sir Arthur Conan Doyle.

At the present moment PF_2-hydrazine chemistry is in a similar situation to that of $PF_2(NR_2)$ chemistry prior to 1971 - although some derivatives are known, such as $PF_2[NMe(NMe_2)]$[256], they are all fully substituted by alkyl groups at the positions not occupied by a PF_2 group. An attempt was made to remedy the situation by trying to synthesise the parent compounds such as $PF_2[NH(NH_2)]$ or $NH(PF_2)[NH(PF_2)]$.

In an analogous manner to the synthesis[32] of $PF_2(NH_2)$, PF_2Br and N_2H_4 were reacted in a double-bulb apparatus, Experimental Section A1:1. The expected reaction was equation A1:1.

$$PF_2Br + 2N_2H_4 \rightarrow PF_2[NH(NH_2)] + N_2H_4.HBr \quad \ldots \text{A1:1.}$$

White clouds formed and were allowed to settle, giving a wet-looking solid. Some liquid was noted in the bulbs. As the vapour pressure of N_2H_4 is very low the entire sample of hydrazine was not vapourized, and the liquid noted is most likely the unreacted N_2H_4 which was recovered. Fractionation yielded some of the

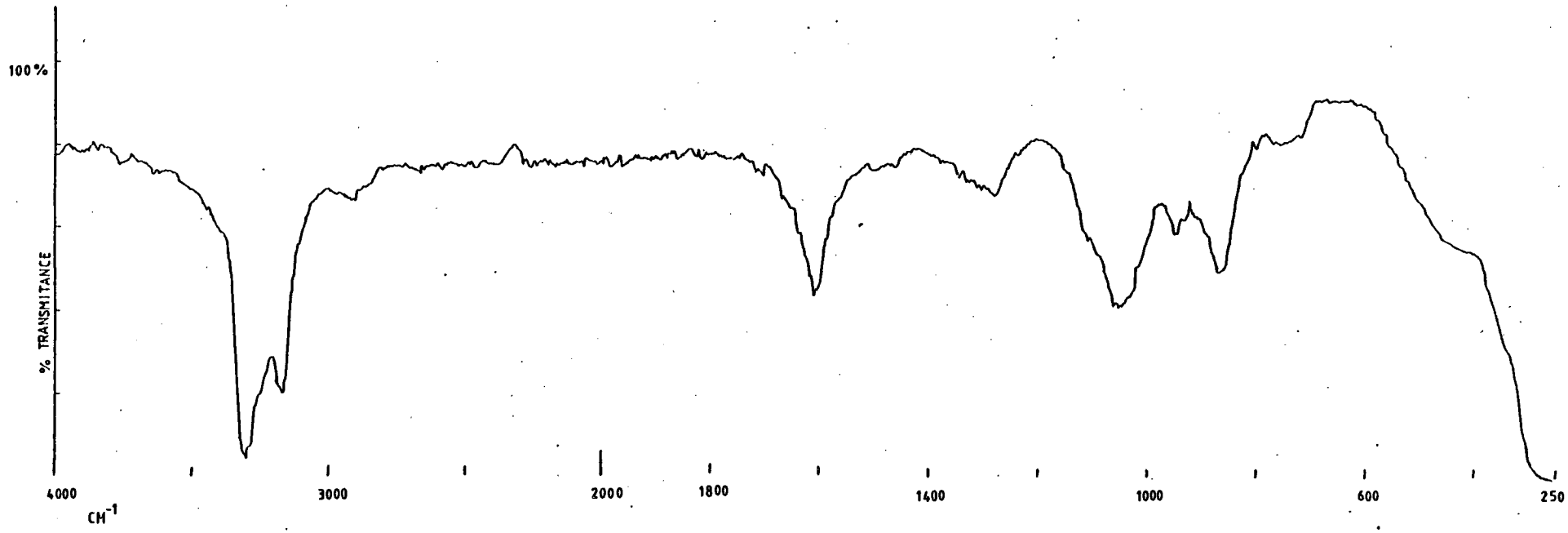


Figure A1:1 Infra red spectrum of the volatile, unidentified, product from the PF_2Br and N_2H_4 reaction.

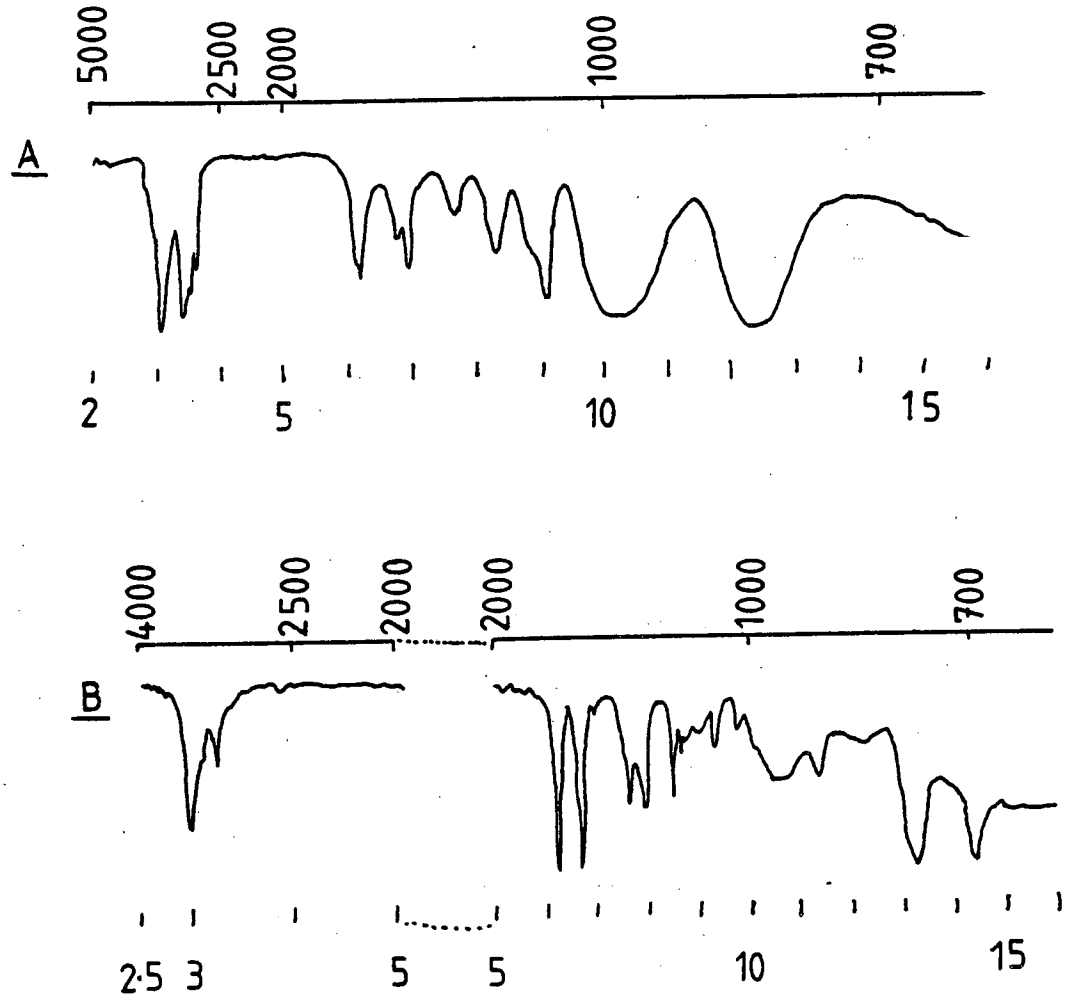


Figure A1:2 Infra red spectra of a) $CH_3[NH(NH_2)]$; b) $Ph[NH(NH_2)]$.

product which was not very volatile and had to be pumped through the traps. The i.r. spectra recorded at various stages were of the same general appearance as those of $NH(R)(NH)_2$ derivatives[257] - Figure A1:1 - and as the PF_2Br was not recovered, it seems that $PF_2[NH(NH_2)]$ may have been made. However, this could not be confirmed by mass spectra of the samples which showed only PF_3, NH_3 and a trace of N_2H_4. Other volatile materials detected by i.r. spectroscopy were PF_3, traces of NH_3, and some N_2H_4, but it was not possible to record a spectrum of the white solid which showed signs of absorbing water when it was exposed to the air. The reaction was repeated but the products fractionated after 3 minutes instead of waiting for the solids to settle. About half the PF_2Br was now recovered as PF_3 but no other products were identified.

The formation of white solids indicates some reaction is occurring and the i.r. spectra provided some evidence that $PF_2[NH(NH_2)]$ may have been formed, but further work is required on this system before any definite conclusions can be drawn. Reactions in n.m.r. tubes would be more fruitful as the nature of the solid might be more readily determined, as well as ensuring that not just the by-products were examined.

Appendix II

Lecture Courses Attended

Year 1973-74

Industrial Research and Development - the Management System (5 lectures) Prof. R.B. Gravenor.

Recent Developments in the Theory of Concerted Processes (5 lectures) Dr. A.J. Bellamy.

Thermal Analysis and Related Techniques (5 lectures) Drs. Lowe and Leach.

Inorganic Colloquia and Seminars.

Year 1974-75

Short Lived Species (5 undergraduate lectures) Dr. R.J. Donovan.

Aspects of Fluorine Chemistry (5 undergraduate lectures) Dr. D.W.H. Rankin.

Some Aspects of Vibrational Spectroscopy (5 lectures) Dr. S. Cradock.

Chemical Aspects of Oil Products Research (5 lectures) Shell Oil Co. Researchers.

Inorganic Colloquia and Seminars.

Year 1975-76

Chemistry of the Upper Atmosphere (6 lectures) Drs. Donovan and Golde.

N.m.r. Spectroscopy (7 lectures) Dr. R.K. Harris.

Inorganic Colloquia and Seminars.

Appendix III

Published Papers

1. E.A.V. Ebsworth, D.W.H. Rankin and John G. Wright, J.C.S. Dalton, 1977, 2348.
Preparation and Spectroscopic Properties of Amines containing Germyl and Difluorophosphino-groups.

2. E.A.V. Ebsworth, D.W.H. Rankin and John G. Wright, J.C.S. Dalton, 1979, 1065.
Preparation and Chemical and Spectroscopic Properties of (Disilylamino)difluorophosphine and Bis(difluorophosphino)silylamine.

3. D.W.H. Rankin and John G. Wright, J.C.S. Dalton, 1979, 1070.
Preparation and Properties of Difluorophosphino-(tetrafluorophosphoranyl)amine.

4. E.A.V. Ebsworth, D.W.H. Rankin, W. Steger and (in part) John G. Wright, J.C.S. Dalton, in press.
Derivatives of Acetamide containing PF_2-groups.

5. D.W.H. Rankin and John G. Wright, J.C.S. Dalton, in press.
Preparation and N.m.r. Spectra of Aminodifluorophosphorane.

Preparation and Spectroscopic Properties of Amines containing Germyl and Difluorophosphino-groups

By E. A. V. Ebsworth, David W. H. Rankin,* and John G. Wright, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1977

Preparation and Spectroscopic Properties of Amines containing Germyl and Difluorophosphino-groups

By E. A. V. Ebsworth, David W. H. Rankin,* and John G. Wright, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The compounds $PF_2[NH(GeH_3)]$, $PF_2[N(GeH_3)_2]$, $PF_2[N(GeH_3)(SiH_3)]$, and $N(GeH_3)(PF_2)_2$ have been prepared from the appropriate primary and secondary difluorophosphinoamines by reaction with germyl halide and trimethylamine. The compounds are all much more stable than trigermylamine, but decompose at room temperature by elimination of GeH_2. Vibrational, photoelectron, n.m.r., and mass spectroscopic data have been recorded, and are interpreted in terms of the probable conformations adopted by the fluorophosphino-groups.

ALTHOUGH trisilylamine is easily prepared [1] and stable at room temperature, the germyl analogue is extremely unstable. Early attempts to prepare it were unsuccessful,[2] and it has subsequently been shown that trigermylamine can be prepared in the gas phase, but that decomposition takes place in a few minutes in the gas phase, and even more rapidly in the liquid phase.[3] The process appears to involve elimination of GeH_2 as a yellow solid, leaving ammonia, which in turn catalyses the decomposition. In contrast, other germanium–nitrogen compounds, such as germyl isocyanate,[4] isothiocyanate,[4] azide,[5] and digermyl carbodi-imide,[6] are reasonably stable in the gas and liquid phases, although there is evidence that these, too, decompose by elimination of GeH_2,[4] as does digermyl ether.[7]

In this paper we describe the preparation and characterisation of four germylamines, stabilised to some extent by the presence of difluorophosphino-substituents on nitrogen. Their properties are compared with those of analogous silylamines [8,9] and simple difluorophosphinoamines.[10,11]

RESULTS AND DISCUSSION

Aminodifluorophosphine and germyl bromide or iodide react to a small extent (1—2%) in the liquid

[1] A. Stock and C. Somieski, *Ber.*, 1921, **54**, 740.
[2] L. M. Dennis and R. W. Work, *J. Amer. Chem. Soc.*, 1933, **55**, 4486
[3] D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1969, 1926.
[4] T. N. Srivastava, J. E. Griffiths, and M. Onyszchuk, *Canad. J. Chem.*, 1962, **40**, 739.
[5] S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1968, 1420.
[6] S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1968, 1423.
[7] T. D. Goldfarb and S. Sujishi, *J. Amer. Chem. Soc.*, 1964, **86**, 1679.
[8] D. E. J. Arnold, E. A. V. Ebsworth, H. F. Jessep, and D. W. H. Rankin, *J.C.S. Dalton*, 1972, 1681.
[9] E. A. V. Ebsworth, D. W. H. Rankin, and J. G. Wright, unpublished work.
[10] D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1971, 783.
[11] D. E. J. Arnold and D. W. H. Rankin, *J.C.S. Dalton*, 1975, 889.

phase, and to an even smaller extent in the gas phase, to give difluoro(germylamino)phosphine [equation (1); X = Br or I]. The small yields contrast with those

$$3PF_2(NH_2) + 2GeH_3X \longrightarrow 2PF_2[NH(GeH_3)] + PF_2X + [NH_4]X \quad (1)$$

obtained in the analogous reaction of $PF_2(NH_2)$ with silyl bromide.[8] However, if the reaction is allowed to proceed in the presence of trimethylamine much greater yields are obtained, and replacement of another hydrogen atom by a germyl group also occurs [equations (2) and (3); X = Br or I]. By changing the reaction conditions, particularly the proportions of $PF_2(NH_2)$ and

$$PF_2(NH_2) + GeH_3X + NMe_3 \longrightarrow PF_2[NH(GeH_3)] + [NHMe_3]X \quad (2)$$

$$PF_2[NH(GeH_3)] + GeH_3X + NMe_3 \longrightarrow PF_2[N(GeH_3)_2] + [NHMe_3]X \quad (3)$$

GeH_3X taken, the relative amounts of germylamines formed can be varied, and pure samples of each compound can be obtained after a lengthy fractionation procedure.

Bis(difluorophosphino)amine does not react directly with germyl iodide in either the gas or the liquid phase, but, on addition of NMe_3, bis(difluorophosphino)germylamine is rapidly formed. The formation of difluoro-

$$NH(PF_2)_2 + GeH_3I + NMe_3 \longrightarrow N(GeH_3)(PF_2)_2 + [NHMe_3]I \quad (4)$$

[germyl(silyl)amino]phosphine from difluoro(silylamino)-phosphine and GeH_3I in the presence of NMe_3 by a similar reaction has been established.

$$PF_2[NH(SiH_3)] + GeH_3I + NMe_3 \longrightarrow PF_2[N(GeH_3)(SiH_3)] + [NHMe_3]I \quad (5)$$

Stability.—Trigermylamine, the other known germylamine, decomposes within a few minutes in the gas phase, unless diluted with an inert gas, and cannot be condensed and revaporised at all.[3] In contrast, the germylamines described here, although less stable than their silyl analogues, are sufficiently stable to be handled by conventional vacuum-line procedures, although in all cases decomposition is faster in glassware not scrupulously dry and clean.

Difluoro(germylamino)phosphine is the least stable of these amines, decomposing completely in the gas phase in *ca.* 1 h at room temperature, and in *ca.* 10 min at 305 K, and having a half-life in the liquid phase at 209 K of *ca.* 15 min. The decomposition involves formation of an involatile yellow solid, the volatile products being mainly $PF_2(NH_2)$, with small amounts of germyl fluoride, monogermane, and digermane. Thus the main route involves GeH_2 elimination, with loss of GeH_3F being of secondary importance. In this respect

$$PF_2[NH(GeH_3)] \longrightarrow PF_2(NH_2) + \frac{1}{n}(GeH_2)_n \quad (6)$$

$$PF_2[NH(GeH_3)] \longrightarrow GeH_3F + \frac{1}{n}(PFNH)_n \quad (7)$$

$PF_2[NH(GeH_3)]$ resembles trigermylamine, rather than $PF_2[NH(SiH_3)]$ whose decomposition gives silyl fluoride.[8] Its instability is such that it is extremely difficult to obtain pure samples, and the spectroscopic data for this compound are therefore incomplete.

(Digermylamino)difluorophosphine is more stable than the monogermyl species, showing no sign of decomposition after 4 h in the gas phase at room temperature. In the liquid phase at 227 K, solid material could be observed after 10 min, and n.m.r. spectra of solutions indicated that the main route involved GeH_2 elimination, giving $PF_2[NH(GeH_3)]$, and then $PF_2(NH_2)$ as in reaction (6).

$$PF_2[N(GeH_3)_2] \longrightarrow PF_2[NH(GeH_3)] + \frac{1}{n}(GeH_2)_n \quad (8)$$

The reason for the extra stability of the digermyl species is not clear: it may be associated with the absence of a N–H bond, or it may reflect reduced basicity of the tertiary amine. The stability of difluoro[germyl(silyl)-amino]phosphine could not be studied, as pure samples were not obtained, but it seemed to be about as stable as the digermyl compound.

Bis(difluorophosphino)germylamine was the most stable compound of the group, remaining unchanged in the gas phase at 305 K for 10 h. Only on prolonged standing in the liquid phase at 209 K did solid materials appear, associated with the formation of $NH(PF_2)_2$: again, loss of GeH_2 is the important breakdown process.

$$N(GeH_3)(PF_2)_2 \longrightarrow NH(PF_2)_2 + \frac{1}{n}(GeH_2)_n \quad (9)$$

The simplest explanation of the observed relative stabilities of the germylamines is that the process is base catalysed, and therefore autocatalytic, with the rates of decomposition being dependent on the amine basicity, which is influenced by the electron-withdrawing character of the substituents, whether by inductive means or by ($p \rightarrow d$) π bonding. Decomposition certainly takes place faster in the presence of NMe_3, and it has been noted that the rate of decay of $N(GeH_3)_3$ accelerates as the more basic ammonia is produced.[3] However, the relative stabilities may also be influenced by intramolecular H–F interactions: in the most probable conformation of $N(GeH_3)(PF_2)_2$, for instance, there would be four short H-F interactions stabilising one GeH_3 group, whereas there would be only two such interactions stabilising two germyl groups in $PF_2[N(GeH_3)_2]$.

N.M.R. Spectra.—N.m.r. parameters for the four germylamines are given in Table 1. Spectra of the compounds with only one PF_2 group were all first order, implying that rotation about P–N bonds must be rapid on the n.m.r. time scale. Complications were introduced by fortuitously equal coupling constants, particularly in the case of $PF_2[^{15}NH'(GeH_3)]$ for which $^2J(^{15}N^1H)$ and $^3J(^{31}P^1H)$ are both 4.6 Hz, and $^3J(^1H^1H')$ and $^4J(^{19}F^1H)$ are both 2.3 Hz. Samples enriched with ^{15}N (*ca.* 95%) were necessary for good ^{31}P spectra to be obtained; in each case, when unenriched samples were used, broad

resonances were observed due to ^{31}P–^{14}N coupling. The proton-decoupled ^{31}P and ^{19}F spectra of $^{15}N(GeH_3)(PF_2)_2$ were second order, representing the A and M parts of an $[A(M)_2]_2X$ spin system.

Chemical shifts for ^{15}N, and signs of coupling constants for $PF_2[^{15}N(GeH_3)_2]$, relative to $^1J(^{31}P^{19}F)$, assumed to be negative, were determined by heteronuclear double-resonance experiments, while observing ^1H spectra. Signs of coupling constants for $^{15}N(GeH_3)(PF_2)_2$ were derived from the analysis of second-order spectra.

TABLE 1

N.m.r. parameters [a]

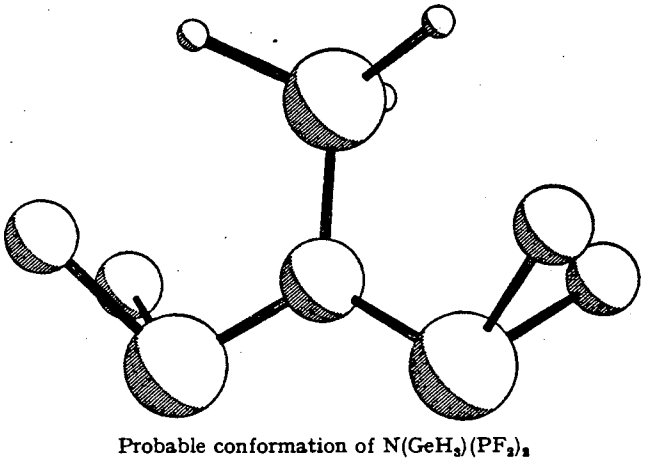
Parameter	$PF_2[^{15}NH'(GeH_3)]$	$PF_2[^{15}N(GeH_3)_2]$	$^{15}N(GeH_3)(PF_2)_2$	$PF_2[N(GeH_3)(SiH'_3)]$
	Compound			
$\delta(^1H)$/p.p.m.	4.82	4.92	4.98	4.95
$\delta(^1H')$/p.p.m.	n.o.			4.35
$\delta(^{19}F)$/p.p.m.	−55.2	−45.8	−60.6	−48.5
$\delta(^{31}P)$/p.p.m.	155.1	158.0	149.8	155.5
$\delta(^{15}N)$/p.p.m. [b]	7.7	−1.4	91.4	n.s.
$^1J(^{31}P^{19}F)$/Hz	1 200	−1 218	−1 239	1 225
$^1J(^{31}P^{15}N)$/Hz	73.5	+82.5	74.0	n.s.
$^2J(^{15}N^1H)$/Hz	4.6	−4.4	3.5	n.s.
$^2J(^{19}F^{15}N)$/Hz	5.6	2.7	4.0	n.s.
$^2J(^{31}P^1H')$/Hz	32.7			
$^2J(^{31}P^{31}P')$/Hz			431 [c]	
$^3J(^{31}P^1H)$/Hz	4.6	+9.4	2.0	n.o.
$^3J(^{19}F^1H')$/Hz	16.3			
$^3J(^1H^1H')$/Hz	2.3			
$^3J(^{31}P^{19}F')$/Hz			+15.7	
$^4J(^{19}F^1H)$/Hz	−2.3	+2.9	3.5	n.o.
$^4J(^{19}F^{19}F')$/Hz			n.o.	
$^4J(^{19}F^{19}F'')$/Hz			n.o.	

Relative signs of coupling constants were determined where they are explicitly given; n.o. = not observed, n.s. = not studied.

[a] Recorded at 223 K for solutions in $CDCl_3$–$SiMe_4$ (1 : 1). [b] Relative to $[NMe_4]I$. [c] Varies from 405 Hz at 303 K to 442 Hz at 193 K.

Chemical shifts for ^1H, ^{19}F, ^{31}P, and ^{15}N are all in the ranges expected. Comparison of parameters reported here with those for the simple difluorophosphinoamines [11] shows that replacement of an amino-hydrogen atom by a germyl group leads to a high-frequency shift of ^{31}P and ^{19}F resonances, but a low-frequency shift of ^{15}N resonance. Replacement of a hydrogen atom by a PF_2 group shifts the resonances in the opposite directions, with the effect on the ^{15}N resonance being much more pronounced, *ca.* 80 p.p.m. The Ge*H* resonances shift to higher frequency with increasing electonegativity of the substituents at N.

Most coupling constants are also as expected, but a few of them call for comment. The value of 32.7 Hz for $^2J(^{31}P^1H)$ in $PF_2[NH(GeH_3)]$ compares with 18.8 Hz in $PF_2[NH(SiH_3)]$[8] and 18.6 Hz in $PF_2(NH_2)$.[10] We suggest that this coupling constant is largest when the phosphorus lone pair eclipses the N–H bond, and therefore that the germyl compound exists in solution predominantly in conformations in which the fluorine atoms are close to the germyl group. In the same compound $^3J(^{31}P^1H)$ is small (4.6 Hz) compared with values for $PF_2[NH(SiH_3)]$ and $PF_2[N(GeH_3)_2]$, and it may be that this coupling is at a maximum when the N–Ge or N–Si bond is eclipsed by the phosphorus lone pair, as has already been suggested [12] for $PCl_2(NMe_2)$. This hypothesis is supported by the observation that $^3J(^{31}P^1H)$ is even smaller (2.0 Hz), in $N(GeH_3)(PF_2)_2$. This compound probably exists in the conformation in which the fluorine atoms are close to the GeH_3 group, so that the phosphorus lone pairs are *trans* to the N–Ge bond (Figure). This conformation also means that two lone pairs are fairly close to each other, giving a large temperature-dependent $^2J(^{31}P^{31}P)$ coupling, as is found in



Probable conformation of $N(GeH_3)(PF_2)_2$

$NMe(PF_2)_2$ [13,14] and other bis(difluorophosphino) compounds.

The coupling constants in $PF_2[NH(SiH_3)]$,[8] $PF_2[N(SiH_3)_2]$, and $N(PF_2)_2(SiH_3)$ [9] can also be interpreted in this way. In the first two compounds the intermediate values of $^3J(PH)$ are regarded as averages of a

[12] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 1085.

[13] J. F. Nixon, *J. Chem. Soc.* (*A*), 1969, 1087.

[14] E. Hedberg, L. Hedberg, and K. Hedberg, *J. Amer. Chem. Soc.*, 1974, **96**, 4417.

large and a small value because of the mixture of conformations. In $N(PF_2)_2(SiH_3)$ the small value for $^3J(PH)$ is due to the predominant conformation. This interpretation implies that the values normally observed for $^2J(PH)$ and $^3J(PH)$ in compounds like these are weighted averages of large and small couplings associated with the two extreme configurations of the lone pairs.

Vibrational Spectra.—Details of the vibrational spectra of the three amines that were isolated and purified are given in Table 2. The compounds must all have low symmetry, and, as the conformations adopted are uncertain, assignments of bands to particular vibrational modes must be tentative. Assignments given in Table 2 are based on typical vibrational frequencies of compounds containing GeH_3 or PF_2 groups. Skeletal modes are therefore suggest that this conformer is relatively stable, a conclusion contradicting our interpretation of the n.m.r. coupling constants. Perhaps the i.r. intensities do not reflect the relative populations of the two conformers; perhaps the solid-phase form of $PF_2[NH(SiH_3)]$ is not equivalent to either of the conformers found in the gas phase. These uncertainties can only be removed by studies of the gas- and solid-phase structures of the compounds involved.

Mass Spectra.—Because of the extreme susceptibility of these compounds to hydrolysis, satisfactory mass spectra were impossible to obtain with our equipment. However, the identities of $PF_2[N(GeH_3)_2]$ and $N(GeH_3)(PF_2)_2$ were confirmed by observation of parent ions, and some of the ions formed by breakdown of the parent.

TABLE 2

Vibrational spectra (cm^{-1})

$PF_2[NH(GeH_3)]$ (I.r., gas)	$PF_2[N(GeH_3)_2]$ (I.r., gas)	$N(GeH_3)(PF_2)_2$ I.r., gas	$N(GeH_3)(PF_2)_2$ Raman, solid	Assignment
3 444m				ν(NH)
3 380w				
2 111s	2 120s	2 138s	2 162m	$\nu(GeH_3)$
2 096 (sh)	2 107s		2 139vs	
1 225s				δ(NH)
1 190m				
	1 005s	961s	955m	ν(PN)
842s	862s	868s	860s	$\nu(PF_2)$, $\delta(GeH_3)$
			840m	
811vs	820vs	812vs	792w	
	774s			$\nu_{sym}(Ge_2N)$?
			770m	$\nu_{asym}(P_2N)$?
642m	655m	641m	648m, br	$\rho(GeH_3)$
		610m	630m, br	
530w		572w	584m, br	ν(GeN)?
			571m, br	
435w	450m	465ms	422s	$\delta(PF_2)$
	393w			$\nu_{asym}(Ge_2N)$?
	308vw	362ms	391s	$\omega(PF_2)$
		313w		
	270w	296w	280w	$\rho(PF_2)$
			262m	δ(GeNP$_2$) and $\tau(PF_2)$
			231vs	
			153w	
			124w	

s = Strong, m = medium, w = weak, v = very, sh = shoulder, and br = broad. Gas-phase spectra were obtained at 298 K, solid-phase spectra at 77 K.

even more uncertain, since there are no similar compounds that could be used for reference purposes, and the extents of coupling between these vibrations and those of the PF_2 groups are also unknown.

Of particular importance are the bands associated with N–H stretching and deformation in the gas-phase i.r. spectrum of $PF_2[NH(GeH_3)]$. In each region two bands are observed, the higher-frequency band being several times more intense than the lower-frequency one. In the spectrum of the analogous silyl compound there are two bands in each region, but the members of each pair are of approximately equal intensity.[8] From studies of the vibrational spectra of the solid phase and of conformers found in the gas phase, it was deduced that the higher-frequency vibration of each pair was associated with a conformation in which the fluorine atoms are close to the amino-hydrogen atom. The intensities of the bands in the spectrum of the germyl compound

The most important route involved elimination of GeH_2, but loss of a PF_2 group also occurred.

TABLE 3

He(I) u.v. photoelectron spectra

Ionisation potential (eV) $PF_2[N(GeH_3)_2]$	Ionisation potential (eV) $N(GeH_3)(PF_2)_2$	Assignment
10.5	10.8	N $2p_z$
11.3	11.0	P $3p_z$
	11.6	
12.5	12.4	$GeH\sigma$
13.2	13.1	$GeN\sigma$
15.1	15.5	$PN\sigma$
16.5	16.0	F $2p_\pi$
	16.8	
17.6	17.4	$PF\sigma$
	18.3	

Photoelectron Spectra.—He(I) u.v. photoelectron spectra were recorded for the two most stable amines, $PF_2[N(GeH_3)_2]$ and $N(GeH_3)(PF_2)_2$, and details are given in Table 3, with assignments made by comparison with

observed ionisation potentials for other compounds.[11,15,16] The nitrogen 2*p* ionisation potentials were smaller than those in the simple fluorophosphinoamines [11] but larger than that in $N(GeH_3)_3$.[15]

EXPERIMENTAL

All the volatile compounds were handled using a Pyrex-glass vacuum system, equipped with 'Sovirel' greaseless taps. Before the easily hydrolysed fluorophosphinoamines could be prepared, all the glassware had to be carefully dried, by allowing silyl chloride vapour to fill the system for a few minutes. Aminodifluorophosphine,[10] difluoro(silylamino)phosphine,[8] bis(difluorophosphino)amine,[11] and germyl halides [17,18] were prepared by published methods.

Infrared spectra were recorded on Perkin-Elmer 225 and 457 spectrometers, using cells equipped with KBr or CsI windows. Raman spectra were obtained using a Cary 83 instrument, with argon-ion 488-nm laser excitation, mass spectra using an A.E.I. MS902 spectrometer operating at 70 eV ionising voltage,* and u.v. photoelectron spectra using a Perkin-Elmer PS16 spectrometer with He(I) (21.22 eV) excitation. N.m.r. spectra were recorded on Varian Associates XL100 and HA100 spectrometers, the latter modified to accept an irradiation frequency provided by a Schlumberger FS30 frequency synthesiser.

Preparations—$PF_2[NH(GeH_3)]$ *and* $PF_2[N(GeH_3)_2]$. A mixture of germyl iodide (1.1 mmol), aminodifluorophosphine (1.0 mmol), and trimethylamine (1.0 mmol) was warmed to room temperature for 20 s, yellow-brown solids being rapidly formed. Repeated fractionation yielded *difluoro(germylamino)phosphine* (0.25), retained at 209 K, *(digermylamino)difluorophosphine* (*ca.* 0.1) retained at 227 K, unchanged $PF_2(NH_2)$ (0.4), and a mixture of mono- and di-germane (0.3 mmol).

In an experiment designed to maximise the yield of the digermylamine, GeH_3I (2.2 mmol) and $PF_2(NH_2)$ (1.0 mmol) were mixed, in a glass ampoule (40 cm^3), and NMe_3 (2.2 mmol) was added in three stages, the ampoule being warmed to room temperature for a few seconds after each addition. Repeated fractionation yielded $PF_2[N(GeH_3)_2]$ (0.3), $PF_2[NH(GeH_3)]$ (0.15), $PF_2(NH_2)$ (0.35), NMe_3 (0.05), and Ge_2H_6 (0.05 mmol).

$N(GeH_3)(PF_2)_2$.—Bis(difluorophosphino)amine (1.8 mmol) and GeH_3I (2.0 mmol) were mixed in a glass ampoule (40 cm^3) and NMe_3 (2.0 mmol) was added in two portions, the reagents being warmed to room temperature for *ca.* 15 s after each addition. Yellow-brown solids were rapidly formed. Fractionation yielded *bis(difluorophosphino)-germylamine*, retained at 209 K, GeH_3I (0.3, retained at 227 K), $NH(PF_2)_2$ (0.6), NMe_3 (0.1), and GeH_4 (0.35 mmol). The recovered starting materials were again treated with more GeH_3I (1.0 mmol) and NMe_3 (0.9 mmol), and the products were fractionated again. The total yield of the desired product after purification was 0.5 mmol, *ca.* 30% based on $NH(PF_2)_2$ taken.

Reaction of $PF_2[NH(SiH_3)]$ *with* GeH_3I.—Difluoro(silylamino)phosphine (0.4 mmol) and GeH_3I (0.4 mmol) were mixed in a glass ampoule (40 cm^3) and NMe_3 (0.4 mmol) was then added. After warming the reagents to room temperature for *ca.* 15 s the volatile products were immediately distilled into an n.m.r. tube. N.m.r. spectra confirmed the presence of *difluoro[germyl(silyl)amino]phosphine*, together with small amounts of $PF_2[NH(SiH_3)]$, $NH(PF_2)_2$, $PF_2(NH_2)$, and $N(GeH_3)(PF_2)_2$. No attempt was made to isolate a pure sample of the amine since the impurities present would all be of similar volatility.

We thank Dr. S. Cradock for assistance in obtaining and interpreting photoelectron spectra, and the S.R.C. for the award of a research studentship (to J. G. W.).

[7/1028 *Received*, 15*th June*, 1977]

* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

[15] S. Cradock and D. W. H. Rankin, *J.C.S. Faraday II*, 1972, 940.

[16] S. Cradock, E. A. V. Ebsworth, W. J. Savage, and R. A. W. Whiteford, *J.C.S. Faraday II*, 1972, 934.

[17] M. F. Swiniarski and M. Onyszchuk, *Inorg. Synth.*, 1974, **15**, 157.

[18] S. Cradock *Inorg. Synth.*, 1974, **15**, 161.

Preparation and Chemical and Spectroscopic Properties of (Disilylamino)-difluorophosphine and Bis(difluorophosphino)silylamine

By E. A. V. Ebsworth, David W. H. Rankin,* and John G. Wright, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1979

Preparation and Chemical and Spectroscopic Properties of (Disilylamino)-difluorophosphine and Bis(difluorophosphino)silylamine

By E. A. V. Ebsworth, David W. H. Rankin,* and John G. Wright, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The compounds $PF_2[N(SiH_3)_2]$ and $N(PF_2)_2(SiH_3)$ have been prepared by the reactions of $SiBrH_3$ and NMe_3 with $PF_2[NH(SiH_3)]$ and $NH(PF_2)_2$ respectively. Vibrational, n.m.r., mass, and photoelectron spectra have been recorded, and chemical properties have been studied. With diborane, $PF_2[N(SiH_3)_2]$ gives the adduct $PF_2[N(SiH_3)_2]\cdot BH_3$ and $N(PF_2)_2(SiH_3)$ gives both mono- and bis-(borane) adducts; n.m.r. spectra of the three borane adducts have been recorded. In reactions with HBr the P–N bonds are attacked preferentially, whereas in reactions with water the cleavage of the Si–N bonds takes place first.

When chloro- or bromo-difluorophosphine reacts with ammonia in the gas or liquid phase the major volatile product is the primary amine, aminodifluorophosphine, and very small amounts of secondary and tertiary amines are formed.[1] Treatment of $PF_2(NH_2)$ with silyl bromide in the liquid phase leads to the formation of difluoro-(silylamino)phosphine, with replacement of just one of the amine hydrogen atoms,[2] although ammonia and halogenosilanes react rapidly to give the completely substituted product, trisilylamine.[3] The reluctance of (difluorophosphino)amines to undergo further substitution may be attributed to the low basicity of the nitrogen atoms, caused by a combination of inductive effects and possible delocalization of nitrogen lone-pair electrons into phosphorus 3*d* orbitals.

We have recently shown that by adding trimethylamine to the reaction systems, secondary and tertiary amines may be prepared, and we have used this technique to synthesize bis(difluorophosphino)amine and tris-(difluorophosphino)amine,[4] and several amines with both difluorophosphino- and germyl substituents.[5]

Tris(difluorophosphino)amine and trisilylamine are both unusually weak bases, and both molecules have been shown by electron-diffraction studies[6-8] to have planar M_3N skeletons. We have therefore synthesized the mixed amines (disilylamino)difluorophosphine and bis(difluorophosphino)silylamine by reaction of $SiBrH_3$ and NMe_3 with $NH(PF_2)_2$ and $PF_2[NH(SiH_3)]$ respectively, and have investigated some of their chemical and spectroscopic properties. We intend to determine their molecular structures, to see whether these molecules also have planar arrangements of the bonds to nitrogen, and also to study the conformations of the difluorophosphino-groups. Preliminary studies indicate that $PF_2[N(SiH_3)_2]$ does have a planar $PNSi_2$ skeleton.

RESULTS AND DISCUSSION

When difluoro(silylamino)phosphine and silyl bromide were mixed in the liquid phase at room temperature no reaction occurred, but with the addition of trimethylamine a rapid reaction took place, even at low temperatures, with the formation of white solid. The volatile products were a mixture of (disilylamino)difluorophosphine and $PF_2[NH(SiH_3)]$, with some silyl fluoride and bromide. The proportion of the disilylamine was increased to close to 100% by treatment of the products of the first stage with a further excess of $SiBrH_3$ and NMe_3.

$$PF_2[NH(SiH_3)] + SiBrH_3 + NMe_3 \longrightarrow PF_2[N(SiH_3)_2] + [NHMe_3]Br \quad (1)$$

Similarly, bis(difluorophosphino)amine and $SiBrH_3$ did not react in the absence of base, but in the presence of NMe_3 a liquid-phase reaction occurred, even at low temperatures, giving a white solid which became orange-brown at room temperature. The main volatile product was bis(difluorophosphino)silylamine, with smaller amounts of $SiBrH_3$, $SiFH_3$, and trifluorophosphine.

$$NH(PF_2)_2 + SiBrH_3 + NMe_3 \longrightarrow N(PF_2)_2(SiH_3) + [NHMe_3]Br \quad (2)$$

Both of the new amines were stable at room temperature in the liquid or gas phase for periods of at least 1 h, but in the presence of the trimethylammonium salts slow decomposition occurred, giving $SiFH_3$ [and some PF_3 from $N(PF_2)_2(SiH_3)$] and involatile products. Both compounds reacted explosively with air.

N.M.R. Spectra.—The ^1H, ^{19}F, and ^{31}P n.m.r. spectra of $PF_2[^{15}N(SiH_3)_2]$ and $^{15}N(PF_2)_2(SiH_3)$ were recorded. Use of ^{15}N-labelled samples was necessary since ^{14}N quadrupolar broadening of lines in ^{31}P (and to a lesser extent in ^1H) spectra was such that small couplings would not have been resolved. Double-resonance experiments for $PF_2[^{15}N(SiH_3)_2]$ enabled $\delta(^{15}N)$ and signs of coupling constants [relative to $^1K(^{31}P^{19}F)$, assumed to be negative] to be determined.

The spectra of $PF_2[^{15}N(SiH_3)_2]$ were all first order, indicating that rotation about the P–N bond was rapid at the temperature of the experiments (223 K). The ^{19}F and ^{31}P spectra of $^{15}N(PF_2)_2(SiH_3)$, being the A and X parts of an $[A[X]_2]_2MQ_3$ spin system, were second order. With ^1H decoupling, these simplify to a pair of $[A[X]_2]_2$ sub-spectra, which could be easily analysed. N.m.r. parameters for both compounds are given in Table 1.

The observed chemical shifts and coupling constants are in general close to the values expected, and provided positive identification of the compounds. The observation of clearly resolved coupling to ^{14}N in the ^{31}P spectra of both of these compounds is surprising, and must mean

TABLE 1

N.m.r. parameters for $PF_2[^{15}N(SiH_3)_2]$ and $^{15}N(PF_2)_2(SiH_3)$

Parameter	$PF_2[^{15}N(SiH_3)_2]$ [a]	$^{15}N(PF_2)_2(SiH_3)$ [b]
$\delta(^1H)$/p.p.m.	4.42	4.39
$\delta(^{19}F)$ [c]/p.p.m.	−51.6	−62.3
$\delta(^{31}P)$ [d]/p.p.m.	155.7	150.0
$\delta(^{15}N)$ [e]/p.p.m.	7.1	n.s.
$^1J(^{31}P^{19}F)$/Hz	−1 237	−1 255
$^1J(^{31}P^{15}N)$/Hz	+77.5 [d]	74.6 [f]
$^1J(^{29}Si^1H)$/Hz	228	232
$^2J(^{19}F^{15}N)$/Hz	−2.6	3.2
$^2J(^{15}N^1H)$/Hz	−3.8	3.5
$^2J(^{31}P^{29}Si)$/Hz	25	7
$^2J(^{31}P^{31}P')$/Hz		367.6
$^3J(^{31}P^1H)$/Hz	+9.3	3.5
$^3J(^{29}Si^{19}F)$/Hz	7.5	11.6
$^3J(^{31}P^{19}F')$/Hz		+24.9
$^4J(^{19}F^1H)$/Hz	+2.9	3.7
$^4J(^{19}F^{19}F')$/Hz		3.7
$^4J(^{19}F^{19}F'')$/Hz		8.0

Relative signs of coupling constants were determined, where they are explicitly given; n.s. = not studied. Chemical shifts are positive to high frequency.

[a] Recorded at 223 K for solutions in CCl_3D–$SiMe_4$ (3 : 1). [b] Recorded at 238 K for solutions in CCl_3D–$SiMe_4$ (3 : 1). [c] Relative to CCl_4F. [d] Relative to 85% H_3PO_4. [e] Relative to $[NMe_4]I$. [f] $^1J(^{31}P^{14}N)$ was observed to be *ca.* 50 Hz.

that the electric-field gradients at the nitrogen atoms are fortuitously small. Both compounds are likely to have trigonal-planar arrangements of the bonds to nitrogen, and it is particularly noteworthy that replacement of a silyl by a difluorophosphino-group does not seem to have a large effect on the linewidths of the ^{31}P resonances. The ^{31}P spectra of other aminodifluorophosphines usually have broad resonances, with no, or poorly resolved, ^{14}N splittings.

It has been suggested [5,9] that some two- or three-bond couplings to three-co-ordinate ^{31}P depend on conformation, with large couplings to nuclei that are *cis* to the phosphorus lone pair of electrons. For $N(PF_2)_2(SiH_3)$, $^3J(^{31}P^1H)$ and $^2J(^{31}P^{29}Si)$ are both very small (3.5 and 7 Hz respectively), and we therefore consider that the conformation adopted by this molecule is probably the same as that proposed for $N(GeH_3)(PF_2)_2$,[5] with the PF_2 groups turned towards the MH_3 group, as has been observed for $NMe(PF_2)_2$,[10] which also has a very small $^3J(^{31}P^1H)$.[11] For $PF_2[N(SiH_3)_2]$ the values of these two couplings are substantially larger (9.3 and 25 Hz respectively), and we suggest that these are the averages of large and small values for nuclei *cis* and *trans* to the phosphorus lone pair, and therefore that there is free exchange (on the n.m.r. time scale) between the two equivalent conformations in which the phosphorus lone pair eclipses one of the N–Si bonds.

The large value of $^2J(^{31}P^{31}P)$ for $N(PF_2)_2(SiH_3)$ is also consistent with the proposed conformation.[12] This coupling constant was found to decrease with increasing temperature (Table 2), consistent with increasing amplitudes of torsional vibrations about the P–N bonds. Other coupling constants change little with temperature, the most significant change observed being of $^3J(^{31}P^{19}F)$, from 27.8 Hz at 293 K to 22.8 Hz at 203 K.

Infrared Spectra.—Details of the gas- and solid-phase i.r. spectra of the two amines are given in Table 3. The assignments of group frequencies given in the Table are very tentative, since the molecules must have low symmetry, and there will be considerable mixing of vibrations, particularly between those of the PF_2 groups and the so-called ' skeletal ' vibrations. However, there are bands in the regions normally associated with the stretching and deformation vibrations of silyl and difluorophosphino-groups, and the spectra are generally similar in appearance to those of their germyl analogues.

Mass Spectra.—Details of the mass spectra of the two amines are given in Table 4. There are at least two breakdown routes for $PF_2[N(SiH_3)_2]$, one involving loss of a silyl group, followed by either HF or a second silyl group, and the other involving loss of a PF_2 group first. In the spectrum of $N(PF_2)_2(SiH_3)$ the parent-ion peak is very weak indeed, and it appears that SiH_2 is eliminated to give $[NH(PF_2)_2]^+$, which can then lose H, F, HF (metastable ion peak observed), PF_2, or PF_3. An alternative route involves initial loss of a PF_2 group, giving $[N(PF_2)(SiH_3)]^+$.

Photoelectron Spectra.—He(I) u.v. photoelectron spectra were recorded, and details are given in Table 5. Assign-

TABLE 2

Temperature variation of $^2J(^{31}P^{31}P)$ in $N(PF_2)_2(SiH_3)$ *

T/K	Coupling (Hz)
203	397.0
233	375.6
263	354.2
293	333.2

* Recorded for solutions in CCl_3D–$SiMe_4$ (3 : 1).

TABLE 3

Infrared spectra (cm^{-1})

$PF_2[N(SiH_3)_2]$		$N(PF_2)_2(SiH_3)$		Assignment
Gas	Solid	Gas	Solid	
2 212s (sh)			2 230m	ν(SiH)
2 189s	2 185s	2 220ms	2 218m	
			2 199m	
			2 178m	
1 930vw		1 946vw		
1 900vw		1 907vw		
		1 638vw		
1 014m	1 034s			
1 004m	1 000mw		992m	δ(SiH$_3$) ν(skeletal)
990s (sh)	958s	963, 954 vs	964s	
970s	927s		935 (sh)	
			918vs	
926vs	893vs	936vs	886 (sh)	
822, 815, 808 s (sh), s	819m	830vs	838m	ν(PF$_2$)
795s	791s	817vs	814s	
			790vs	
			774 (sh)	
734mw	751s	751w	736m	ρ(SiH$_3$)
	730s (sh)	713w	705w	
674w	685w	656w	660w	ν(skeletal)
529w	532, 523 w	548w		
			478w	
		465m	462m	δ(PF$_2$)
			447w	
			431w	
			408w	
368, 362 vw	357m	362m	367s	δ- or ω-(PF$_2$)
325mw	326, 319 m, w (sh)	348 (sh), 291, 282 w	357m	
				ω- or ρ-(PF$_2$)

TABLE 4

Mass spectra

m/e	Relative abundance $PF_2[N(SiH_3)_2]$	Relative abundance $N(PF_2)_2(SiH_3)$	Assignment
183		0.2	$[N(PF_2)_2(SiH_3)]^+$
153		73	$[NH(PF_2)_2]^+$
152		41	$[N(PF_2)_2]^+$
145	59		$[PF_2\{N(SiH_3)_2\}]^+$
134		10	$[NH(PF_2)(PF)]^+$
133		34	$[N(PF_2)(PF)]^+$
115	20		$[NH(PF_2)(SiH_3)]^+$
114	100	24	$[N(PF_2)(SiH_3)]^+$
113	85		$[N(PF_2)(SiH_2)]^+$
112	59	8	$[N(PF_2)(SiH)]^+$
94	56		$[PF(NSiH_2)]^+$
93	7		$[PF(NSiH)]^+$
92	18		$[PF(NSi)]^+$
88		6	$[PF_2]^+$
85	21	9	$[PF_2(NH_2)]^+$
78	21	7	$[O(SiH_3)_2]^+$
77	34	60	$[NH(SiH_3)_2]^+$, $[PH(NSiH_3)]^+$
76	56	24	$[N(SiH_3)_2]^+$, $[P(NSiH_3)]^+$
75	27	33	$[N(SiH_3)(SiH_2)]^+$, $[P(NSiH_2)]^+$
74	19	5	$[N(SiH_2)_2]^+$, $[P(NSiH)]$
73	20	15	$[N(SiH_2)(SiH)]^+$, $[P(NSi)]^+$
72	17	6	$[N(SiH)_2]^+$
70	25		$[NSi_2]^+$
69	33	100	$[PF_2]^+$
65		66	$[PF(NH)]^+$
50	4	8	$[PF]^+$, $[SiFH_3]^+$
49	22	23	$[SiFH_2]^+$
48	8	14	$[SiFH]^+$
47	22	7	$[SiF]^+$
46	59	48	$[PNH]^+$, $[NH(SiH_3)]^+$
45	15		$[PN]^+$, $[NSiH_3]^+$
42	9		$[NSi]^+$
31		12	$[SiH_3]^+$
29	8		$[SiH]^+$
28	8	5	$[Si]^+$

Only ions of abundance >5% of that of the most abundant ion are included.

TABLE 5

He(I) photoelectron spectra

Ionization potential/eV $PF_2[N(SiH_3)_2]$	Ionization potential/eV $N(PF_2)_2(SiH_3)$	Assignment
10.8		N $2p_z$, P $3p_z$
	11.2	N $2p_z$
	11.7, 12.2	P $3p_z$
12.3, 12.7	13.5	SiH_σ
13.7	14.3	SiN_σ
15.2	15.6	PN_σ
16.7	16.1, 16.8	F $2p_\pi$
17.8	17.5, 18.4	PF_σ

ments were made by comparison with observed ionization potentials for other aminodifluorophosphines [4,5,13] and silylamines.[14] The spectra are generally very similar to those of the germyl analogues, in peak positions and areas. We therefore assign both nitrogen and phosphorus lone-pair levels of $PF_2[N(SiH_3)_2]$ to 10.8 eV,* and conclude that the axes of the two lone pairs must be orthogonal. This is consistent with the conformation proposed on the basis of n.m.r. coupling constants. No conclusions may be drawn concerning the conformation of $N(PF_2)_2(SiH_3)$, since three distinct bands are seen in the 10—12.5 eV region.

It should be noted that the nitrogen lone-pair ionization potentials of these silylamines are *ca.* 0.4 eV larger than those of their germyl analogues,[5] this difference being close to that between the potentials of trisilyl- and trigermyl-amines.[14]

Reactions with HBr *and Water.*—When equimolar amounts of $N(PF_2)_2(SiH_3)$ and HBr were allowed to react in an n.m.r. tube the products were $PBrF_2$, $SiBrH_3$, a white solid, and unchanged amine. Since $NH(PF_2)_2$ is known not to react rapidly with HBr,[4] it follows that a P–N bond must have been broken first to give $PF_2[NH(SiH_3)]$, which is known to react further.[2] Similarly, reaction of equimolar amounts of $PF_2[N(SiH_3)_2]$ and HBr gave $PBrF_2$ and $SiBrH_3$ in a ratio of *ca.* 2 : 1, with disilylamine and unchanged tertiary amine. In this case also the P–N bond appears to be attacked preferentially.

In contrast to this, however, $PF_2[N(SiH_3)_2]$ reacted with water to give $PF_2[NH(SiH_3)]$, $PF_2(NH_2)$, PF_3, $O(PF_2)_2$, $O(SiH_3)_2$, SiH_4, $SiFH_3$, all identified by n.m.r. spectroscopy, and solid products, while $N(PF_2)_2(SiH_3)$ gave the same products, with $NH(PF_2)_2$ instead of $PF_2[NH(SiH_3)]$. The initial reaction in both cases is therefore cleavage of an Si–N bond.

Exchange Reactions of $PF_2[N(SiH_3)_2]$.—When $PF_2[N(SiH_3)_2]$ was treated with $PBrF_2$ at room temperature slow decomposition took place, and although a little $SiBrH_3$ was formed no $N(PF_2)_2(SiH_3)$ or $N(PF_2)_3$ was observed. Similarly, there was no reaction with PF_3O, nor between PF_3O and $N(PF_2)_2(SiH_3)$. With PF_5, however, a rapid reaction occurred, giving $PF_2(N{=}PF_3)$, identified by its n.m.r. parameters. Presumably, this is formed by a substitution reaction, followed by elimination of $SiFH_3$ [equations (3) and (4)]. A reaction

$$PF_2[N(SiH_3)_2] + PF_5 \longrightarrow SiFH_3 + PF_2[N(PF_4)(SiH_3)] \quad (3)$$

$$PF_2[N(PF_4)(SiH_3)] \longrightarrow SiFH_3 + PF_3(NPF_3) \quad (4)$$

analogous to the first part of this has been observed for $PF_2[NH(SiH_3)]$ and PF_5.[15]

Reaction of $PF_2[N(SiH_3)_2]$ *with Sulphur.*—The oxidation of $PF_2(NMe_2)$ to $PF_2(NMe_2)(S)$ by sulphur can be achieved, but the reaction takes *ca.* 5 d at 420 K. The analogous oxidation reaction of $PF_2[N(SiH_3)_2]$ was attempted, but complete decomposition of the amine occurred within 24 h at 360 K, and no phosphorus(v) products were observed.

Reactions with Diborane.—When $PF_2[N(SiH_3)_2]$ and diborane were allowed to warm to room temperature in solution in CCl_3H an immediate and quantitative reaction occurred. The product, which was stable at room temperature in solution, was unequivocally identi-

* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

TABLE 6

N.m.r. parameters for borane adducts of $PF_2[N(SiH_3)_2]$ and $N(PF_2)_2(SiH_3)$

Parameter	$PF_2[^{15}N(SiH'_3)_2]\cdot BH_3$ [a]	$PF_2[N(P'F'_2)(SiH'_3)]\cdot BH_3$ [b]	$N[PF_2(BH_3)]_2(SiH'_3)$ [b]
$\delta(^1H)$/p.p.m.	0.78	n.o.[c]	n.o.[c]
$\delta(^1H')$/p.p.m.	4.47	n.o.[c]	n.o.[c]
$\delta(^{19}F)$ [d]/p.p.m.	−60.2	−64.4	−60.7
$\delta(^{19}F')$ [d]/p.p.m.		−60.2	
$\delta(^{31}P)$ [e]/p.p.m.	135.1	130.7	128.9
$\delta(^{31}P')$ [e]/p.p.m.		142.6	
$^1J(^{31}P^{19}F)$/Hz	1 209	1 205	1 250[f]
$^1J(^{31}P'^{19}F')$/Hz		1 288	
$^1J(^{31}P^{15}N)$/Hz	40.9	n.s.	n.s.
$^1J(^{31}P^{11}B)$/Hz	72.4	55	n.o.[c]
$^1J(^{29}Si^1H')$/Hz	212	n.o.	n.o.
$^1J(^{11}B^1H)$/Hz	101	100	100
$^2J(^{31}P^1H)$/Hz	16	n.o.	n.o.
$^2J(^{15}N^1H')$/Hz	4.2	n.s.	n.s.
$^2J(^{31}P^{31}P')$/Hz		118	<10
$^3J(^{19}F^1H)$/Hz	16	17	16
$^3J(^{31}P^1H')$/Hz	6.9	n.o.	n.o.
$^4J(^{19}F^1H')$/Hz	2.1	n.o.	n.o.

n.o. = Not observed, n.s. = not studied. Chemical shifts are positive to high frequency.

[a] Solution in CCl_3D at 303 K. [b] Solution in CCl_3D at 223 K. [c] Not resolved, see text. [d] Relative to CCl_3F. [e] Relative to 85% H_3PO_4. [f] $|^1J(PF) + {}^3J(PF')|$; $^3J(PF) < 5$ Hz.

fied from n.m.r. spectra as an adduct, with a borane group co-ordinated to the phosphorus atom. The ^{31}P spectra were particularly useful, since couplings to ^{19}F, ^{11}B, ^{15}N, and two types of protons could be observed. Couplings to the quadrupolar ^{11}B nuclei were clearly resolved in ^1H and ^{31}P spectra, but the resonances were broad and some small couplings could not be observed. With the ^{14}N species the ^{31}P spectrum was very poorly resolved, and ^{15}N substitution was essential so that the multiplicities of the resonances, and hence the identity of the species, could be reliably established. No attempt was made to isolate the adduct.

$$2PF_2[N(SiH_3)_2] + B_2H_6 \longrightarrow 2PF_2[N(SiH_3)_2]\cdot BH_3 \quad (5)$$

Several reactions of $N(PF_2)_2(SiH_3)$ with diborane were carried out, using different ratios of reagents. Spectra were recorded at 223 K, after briefly warming the mixture to room temperature, and two different complexes were detected in each case. Neither was stable at room temperature.

The complex that was formed first was identified by n.m.r. spectroscopy as the mono(borane) species, $PF_2[N(PF_2)(SiH_3)]\cdot BH_3$. The ^{31}P spectrum contained two sets of resonances, both apparently first order, each with coupling to two ^{19}F nuclei and to each other, with one set showing coupling to a ^{11}B nucleus. The ^{19}F spectrum similarly contained two sets of resonances, one of which showed coupling to three protons, but these resonances were second order and were not fully analysed. The second-order features indicate that the two fluorine atoms on one phosphorus atom are not magnetically equivalent, which implies that rotation about the P–N bond is restricted.

The second complex formed was the major ultimate product, even when excess of amine was used in the reaction. It was identified as the bis(borane) complex, $N[PF_2(BH_3)]_2(SiH_3)$. Both ^{19}F and ^{31}P n.m.r. spectra of this species showed that there was only one type of PF_2 group present, with couplings to co-ordinated BH_3 groups, but both spectra were second-order centrosymmetric patterns, as would be expected for $[PF_2(BH_3)]_2$ spin systems. With broadening due to ^{14}N and ^{11}B, the spectra were exceedingly complex, and a full analysis was not attempted.

Proton n.m.r. spectra of the complexes contained resonances that could be assigned to silyl and co-ordinated borane groups, but since the complicated patterns of the two species present in every sample overlapped the chemical shifts and coupling constants could not be determined reliably.

The preferred formation of a complex containing two co-ordinated borane groups is of interest, since other systems with two PF_2 groups, such as P_2F_4,[16] $O(PF_2)_2$,[17] $S(PF_2)_2$,[18] and $Se(PF_2)_2$,[12] have only accepted a single borane. In the cases of P_2F_4 and the sulphur and selenium compounds this may be attributed to steric factors, but it seems unlikely that the same could be true for the oxygen compound which has a wide angle at oxygen when uncomplexed.[19] Our preliminary studies of other amines with two PF_2 groups indicate that these also can co-ordinate to two borane groups.[20]

N.m.r. parameters for the three borane complexes are given in Table 6. They are in general fully consistent with those reported for related compounds. The measured values of $^1J(^{31}P^{11}B)$ are somewhat smaller than those in alkyl(difluorophosphino)amine complexes,[21] while $\delta(^1H)$ is somewhat larger,[22] and this implies that the phosphine basicity is reduced by the silyl substituents.

The coupling $^1J(^{31}P^{15}N)$ in $PF_2[N(SiH_3)_2]\cdot BH_3$ (41 Hz) is intermediate in magnitude between those in phosphorus(III) and four-co-ordinate phosphorus(V) compounds. We conclude that the sign of this coupling is probably positive, as in phosphorus(III) compounds.

The two-bond phosphorus–phosphorus coupling is also interesting, changing from *ca.* 350 Hz in complexed $N(PF_2)_2(SiH_3)$ to 118 Hz in the mono(borane) complex, and to <10 Hz in the bis(borane) species. This change

is consistent with the idea that large $^2J(^{31}P^{31}P)$ couplings are found in systems in which two phosphorus lone pairs of electrons can interact.

EXPERIMENTAL

All volatile compounds were handled in a Pyrex-glass vacuum line, equipped with 'Sovirel' poly(tetrafluoroethylene) taps. All glass apparatus was dried by allowing contact with silyl chloride vapour for a period of several minutes. Silyl bromide,[23] $PF_2[NH(SiH_3)]$,[3] $NH(PF_2)_2$,[4] and diborane [24] were prepared by standard literature methods.

Proton n.m.r. and double-resonance experiments were carried out using a Varian Associates HA100 spectrometer, modified [25] to accept a second radiofrequency derived from a Schlumberger FS30 frequency synthesizer. Fluorine-19 and ^{31}P spectra were obtained using a Varian Associates XL100 spectrometer with deuterium lock and Gyrocode decoupler. Infrared spectra were recorded in the range 200—4 000 cm^{-1} on Perkin-Elmer 225 and 457 spectrometers, using cells equipped with KBr or CsI windows. Mass spectra were obtained using an A.E.I. MS902 spectrometer operating at 70 eV ionizing voltage, and u.v. photoelectron spectra using a Perkin-Elmer PS16 spectrometer with He(I) (21.22 eV) excitation.

Preparations.—*(Disilylamino)difluorophosphine.*—In a typical experiment, NMe_3 (2.4 mmol) was condensed into a glass ampoule (40 cm^3) containing a mixture of $PF_2[NH(SiH_3)]$ (2.2 mmol) and $SiBrH_3$ (2.5 mmol). After briefly warming the reagents to room temperature the products were fractionated, and the portion volatile at 177 K was discarded, leaving 2.0 mmol of an 85 : 15 mixture of $PF_2[N(SiH_3)_2]$ and $PF_2[NH(SiH_3)]$. This mixture was then treated with more portions of $SiBrH_3$ (1.0 mmol) and NMe_3 (0.8 mmol), and on fractionation it yielded (disilylamino)difluorophosphine (1.7 mmol, 77%), volatile at 195 K but retained at 177 K.

In the same way $PF_2[^{15}N(SiH_3)_2]$ was prepared from $PF_2[^{15}NH(SiH_3)]$, which was made from $PF_2(^{15}NH_2)$, which in turn was obtained from $^{15}NH_3$.

Bis(difluorophosphino)silylamine. Trimethylamine (1.0 mmol) was condensed into a glass ampoule (40 cm^3) containing a mixture of $NH(PF_2)_2$ (0.8 mmol) and $SiBrH_3$ (1.2 mmol). The reagents were warmed to room temperature for 15 s, with the formation of first white and then orange-brown solids. Fractionation of the volatile products yielded bis(difluorophosphino)silylamine (0.7 mmol, 87%), involatile at 177 K but volatile at 195 K.

Similarly, $^{15}N(PF_2)_2(SiH_3)$ was prepared from $^{15}NH(PF_2)_2$, which was made from $^{15}NH_3$ and $PBrF_2$ in the usual manner.

Reactions of $PF_2[N(SiH_3)_2]$ *and of* $N(PF_2)_2(SiH_3)$.—*With* HBr. The reactions were carried out in CCl_3D solution in n.m.r. tubes and were monitored by ^1H and ^{31}P n.m.r. spectroscopy. In a typical experiment, $PF_2[N(SiH_3)_2]$ (0.3 mmol) and HBr (0.3 mmol) were allowed to react at room temperature, with the formation of $PBrF_2$, $SiBrH_3$, and a white solid.

With water. These reactions were also carried out in n.m.r. tubes. The amounts of water introduced were not accurately measured, but small quantities could be added either by passing the amine through glass tubing which had previously been in contact with water vapour, or by using CCl_3D solvent which had not been carefully dried before use.

With $PBrF_2$. In an n.m.r. tube, $PF_2[N(SiH_3)_2]$ (0.25 mmol) and $PBrF_2$ (0.6 mmol) were allowed to stand at room temperature for 24 h. Proton and ^{31}P n.m.r. spectra showed that decomposition was taking place, with no displacement of silyl by PF_2 groups.

With sulphur. When sulphur (0.075 g) was heated with $PF_2[N(SiH_3)_2]$ in CCl_3D solution, ^1H and ^{31}P n.m.r. spectra showed that decomposition of the amine occurred, without the formation of any phosphorus(v) species.

With PF_5. Equimolar quantities of $PF_2[N(SiH_3)_2]$ and PF_5 were allowed to react in CCl_3D solution in an n.m.r. tube. The tube was warmed to room temperature for a few minutes, and ^{31}P n.m.r. spectra were then recorded at 223 K. These indicated that $PF_2(NPF_3)$ had been formed.

With PF_3O. When PF_3O was warmed to room temperature with $PF_2[N(SiH_3)_2]$ or $N(PF_2)_2(SiH_3)$ in CCl_3D solution, no reaction occurred other than the slow decomposition of the amine.

With B_2H_6. Reactions between $PF_2[N(SiH_3)_2]$ or $N(PF_2)_2(SiH_3)$ and B_2H_6 were carried out in CCl_3D solution in n.m.r. tubes. Samples were warmed to room temperature to allow reaction to occur, and spectra were then recorded at room temperature or at 223 K, depending on the stability of the products.

We thank Dr. S. Cradock for assistance in recording and interpreting photoelectron spectra, and the S.R.C. for the award of a research studentship (to J. G. W.).

[8/1192 *Received, 29th June*, 1978]

REFERENCES

1 D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1971, 783.
2 D. E. J. Arnold, E. A. V. Ebsworth, H. F. Jessep, and D. W. H. Rankin, *J.C.S. Dalton*, 1972, 1681.
3 A. Stock and C. Somieski, *Ber.*, 1921, **54**, 740.
4 D. E. J. Arnold and D. W. H. Rankin, *J.C.S. Dalton*, 1975, 889.
5 E. A. V. Ebsworth, D. W. H. Rankin, and J. G. Wright, *J.C.S. Dalton*, 1977, 2348.
6 D. E. J. Arnold, D. W. H. Rankin, M. R. Todd, and R. Seip, *J.C.S. Dalton*, in the press.
7 K. Hedberg, *J. Amer. Chem. Soc.*, 1955, **71**, 6491.
8 B. Beagley and A. R. Conrad, *Trans. Faraday Soc.*, 1970, **66**, 2740.
9 A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 1085.
10 E. Hedberg, L. Hedberg, and K. Hedberg, *J. Amer. Chem. Soc.*, 1974, **96**, 4417.
11 J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2689.
12 D. E. J. Arnold, E. R. Cromie, and D. W. H. Rankin, *J.C.S. Dalton*, 1977, 1999.
13 S. Cradock and D. W. H. Rankin, *J.C.S. Faraday II*, 1972, 940.
14 S. Cradock, E. A. V. Ebsworth, W. J. Savage, and R. A. Whiteford, *J.C.S. Faraday II*, 1972, 934.
15 D. W. H. Rankin and J. G. Wright, following paper.
16 K. W. Morse and R. W. Parry, *J. Amer. Chem. Soc.*, 1966, **88**, 3729.
17 L. F. Centofanti and R. W. Parry, *Inorg. Chem.*, 1968, **7**, 1005.
18 G. N. Bockermann and R. W. Parry, *J. Fluorine Chem.*, 1976, **7**, 1.
19 D. E. J. Arnold and D. W. H. Rankin, *J. Fluorine Chem.*, 1972, **2**, 405; Hsuikang Yu Yow, R. W. Rudolph, and L. S. Bartell, *J. Mol. Structure*, 1975, **28**, 205.
20 A. W. Burt and D. W. H. Rankin, unpublished work.
21 R. W. Rudolph and C. W. Schultz, *J. Amer. Chem. Soc.*, 1971, **93**, 6821.
22 A. H. Cowley and M. C. Damasco, *J. Amer. Chem. Soc.*, 1971, **93**, 6815.
23 L. G. L. Ward, *Inorg. Synth.*, 1968, **11**, 159.
24 A. D. Norman and W. L. Jolly, *Inorg. Synth.*, 1968, **11**, 15.
25 A. Charles and W. McFarlane, *Mol. Phys.*, 1968, **14**, 299.

Preparation and Properties of Difluorophosphino(tetrafluorophosphoranyl)amine

By David W. H. Rankin * and John G. Wright, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1979

Preparation and Properties of Difluorophosphino(tetrafluorophosphoranyl)amine

By David W. H. Rankin * and John G. Wright, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The compound $NH(PF_2)(PF_4)$ has been prepared from $PF_2[NH(SiH_3)]$ by reaction with PF_5. Vibrational, photoelectron, n.m.r., and mass spectroscopic data have been recorded, and interpreted in terms of the probable structure and conformation of the molecule. At low temperatures the phosphorus(v) group has chemically equivalent equatorial fluorine atoms but non-equivalent axial atoms, indicating restricted rotation about the P–N bond as well as restricted pseudo-rotation. At high temperatures, all four fluorine atoms are equivalent.

THE combination of phosphorus(III) and phosphorus(V) atoms in a single compound is well known, and examples have been reported in which the two phosphorus atoms are linked by oxygen,[1] sulphur,[1] or nitrogen.[2] In most of these cases, however, the P^V is four-co-ordinate, and the conjunction of three co-ordinate P^{III} with five-co-ordinate P^V is a much rarer phenomenon.

A number of fairly stable aminofluorophosphoranes are known,[3-5] and we have prepared a variety of secondary amines containing difluorophosphino-groups.[6-8] We therefore considered that the mixed-valence amine $NH(PF_2)(PF_4)$ should be accessible. It is well known that fluorosilane elimination provides a useful route to substituted fluorophosphoranes,[9,10] and so we have studied the reaction of $PF_2[NH(SiH_3)]$ with phosphorus pentafluoride, and have successfully prepared $NH(PF_2)(PF_4)$. While this work was in progress, the preparation of $NMe(PF_2)(PF_4)$ by a similar route was reported.[2]

RESULTS AND DISCUSSION

When equimolar amounts of $PF_2[NH(SiH_3)]$ and PF_5 were allowed to mix in the liquid phase at room temperature a rapid reaction occurred, giving fluorosilane and difluorophosphino(tetrafluorophosphoranyl)amine [equation (1)]. Trifluorophosphine, $PF_2(NPF_3)$, and a white

$$PF_2[NH(SiH_3)] + PF_5 \longrightarrow NH(PF_2)(PF_4) + SiFH_3 \quad (1)$$

solid were also formed, but in very small amounts, and yields of up to 95% of the desired product were obtained. Attempts to prepare the amine by direct reaction of $PF_2(NH_2)$ and PF_5 were unsuccessful, and an involatile white solid was the only significant product. The nature of this solid was not acertained, but reactions of $NH(PF_2)(PF_4)$ with HBr or HCl lead to the slow formation of similar white solids, and it seems probable that they are adducts, since both phosphorus atoms and the nitrogen atom are potential donor or acceptor sites.

Difluorophosphino(tetrafluorophosphoranyl)amine is a colourless, mobile, volatile liquid, stable in the gas and liquid phases at temperatures up to at least 375 K over several hours. At higher temperatures, $PF_2(NPF_3)$ is slowly formed, and a white solid is deposited. The decomposition reaction was accelerated markedly when samples were irradiated with green (488 nm) light during a laser Raman experiment, but samples were stable when a red (647 nm) laser was used. Hydrolysis of the amine took place rapidly, giving $O(PF_2)_2$, PF_3O, and a white solid.

Attempts to prepare other mixed-valence secondary amines have been unsuccessful. Reactions of $PF_2[NH(SiH_3)]$ with PF_3O, PF_3S, $PClF_2S$, and $PF_2I(S)$ have all been studied but in each case complete decomposition of the silylamine was observed, without any evidence for the occurrence of substitution reactions.

N.M.R. Spectra.—The ^{31}P, ^{19}F, and ^1H n.m.r. spectra provided unequivocal identification of $NH(PF_2)(PF_4)$. Samples labelled with ^{15}N were used throughout since ^{14}N quadrupolar coupling broadened lines in ^{31}P and ^1H spectra so much that many couplings could not be resolved.

At low temperatures, the ^{19}F spectra contained four sets of resonances, all of first order, with relative intensity 2 : 2 : 1 : 1, which could be assigned, on the basis of multiplicities (Table 1) and magnitudes (Table 2) of

TABLE 1

Couplings and multiplicities in n.m.r. spectra of $^{15}NH(P'F'_2)(PF_4)$

Nucleus	Low temperature	High temperature
^{31}P	$3 \times 2 \times 2 \times 2 \times 2 \times 3 \times 2$ $F_e\ F_a\ F_b\ N\ P'\ F'\ H$	$5 \times 2 \times 2 \times 3 \times 2$ $F\ N\ P'\ F'\ H$
$^{31}P'$	$3 \times 2 \times 2 \times 2 \times 2 \times 2$ $F'\ F_b\ N\ P\ F_a\ H$	$3 \times 2 \times 5 \times 2 \times 2$ $F'\ N\ F\ P\ H$
$^{19}F_a$	$2 \times 3 \times 2 \times 2 \times 2$ $P\ F_e\ P'\ N\ H$	
$^{19}F_b$	$2 \times 2 \times 3 \times 2 \times 3 \times 2$ $P\ P'\ F_e\ H\ F'\ N$	$2 \times 2 \times 3 \times ?$ * $P\ P'\ F'$
$^{19}F_e$	$2 \times 2 \times 2$ $P\ F_a\ F_b$	
$^{19}F'$	$2 \times 2 \times 2 \times 2 \times 2$ $P'\ P\ F_b\ N\ H$	$2 \times 2 \times 5 \times 2 \times 2$ $P'\ P\ F\ N\ H$
^1H	$2 \times 2 \times 3 \times 2 \times 2 \times 2$ $N\ F_a\ F'\ F_b\ P\ P'$	

* Fully resolved high-temperature spectra were not obtained.

couplings, to the fluorine atoms F', F_a, F_b, and F_e (Figure). The observation of three chemically distinct types of fluorine in the PF_4 group implies that not only is pseudo-rotational exchange between axial and equatorial sites slow on the n.m.r. time scale, but also that rotation about the P–N bond is restricted, so that the two axial

TABLE 2

N.m.r. parameters [a] of $^{15}NH(PF_2)(PF_4)$

Parameter		Parameter	
$\delta(^1H)$/p.p.m.	5.40 [b]	$^2J(^{19}F_a-^{19}F_b)$/Hz	<0.2
$\delta(^{31}P)$/p.p.m.	−71.3	$^2J(^{19}F_a-^{19}F_c)$/Hz	88.2
$\delta(^{31}P')$/p.p.m.	138.9	$^2J(^{19}F_b-^{19}F_c)$/Hz	79.7
$\delta(^{19}F_a)$/p.p.m.	−48.3	$^2J(^{19}F_a-^{15}N)$/Hz	11.5
$\delta(^{19}F_b)$/p.p.m.	−41.8	$^2J(^{19}F_b-^{15}N)$/Hz	3.9
$\delta(^{19}F_c)$/p.p.m.	−73.4	$^2J(^{19}F_c-^{15}N)$/Hz	<0.2
$\delta(^{19}F')$/p.p.m.	−61.2	$^2J(^{19}F'-^{15}N)$/Hz	3.4
$\delta(^{15}N)$/p.p.m.	60	$^2J(^{31}P-^{19}F')$/Hz	16.1
$^1J(^{31}P-^{19}F_a)$/Hz	801.7	$^2J(^{31}P'-^{19}F_a)$/Hz	±14.7
$^1J(^{31}P-^{19}F_b)$/Hz	766.5	$^2J(^{31}P'-^{19}F_b)$/Hz	∓209.2
$^1J(^{31}P-^{19}F_c)$/Hz	965.5	$^2J(^{31}P'-^{19}F_c)$/Hz	<0.2
$^1J(^{31}P'-^{19}F')$/Hz	1 256.7	$^3J(^{19}F_a-^1H)$/Hz	1.0
$^1J(^{31}P-^{15}N)$/Hz	69.5	$^3J(^{19}F_b-^1H)$/Hz	31.0
$^1J(^{31}P'-^{15}N)$/Hz	84.0	$^3J(^{19}F_c-^1H)$/Hz	<0.2
$^1J(^{15}N-^1H)$/Hz	80.7 [b]	$^3J(^{19}F'-^1H)$/Hz	6.3
$^2J(^{31}P-^{31}P')$/Hz	14.7	$^4J(^{19}F_a-^{19}F')$/Hz	<0.2
$^2J(^{31}P-^1H)$/Hz	1.0 [b]	$^4J(^{19}F_b-^{19}F')$/Hz	14.0
$^2J(^{31}P'-^1H)$/Hz	1.0 [b]	$^4J(^{19}F_c-^{19}F')$/Hz	<0.2

[a] In CD_2Cl_2–$SiMe_4$ at 223 K, except where indicated otherwise. [b] Measured at 187 K in $CDCl_3$.

fluorine atoms are chemically non-equivalent. Similarly, the ^{31}P spectra run at low temperatures showed two sets of resonances, with chemical shifts as expected for PF_4N and PF_2N species. These resonances were split by the other spinning nuclei in the molecule, with one of them showing coupling to all the seven other groups of nuclei, giving 288 lines in all. The ^1H spectrum also showed six couplings to the single proton.

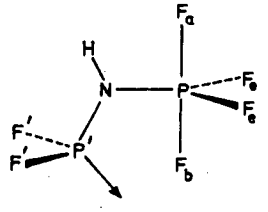


FIGURE Probable structure of $NH(PF_2)(PF_4)$ showing axis of phosphorus lone pair of electrons

A variable-temperature n.m.r. study was initiated, using samples dissolved in a mixture of CD_2Cl_2 and $SiMe_4$. These samples had sharp low-temperature-limiting ^{19}F and ^{31}P spectra at 223 K, but on warming above this temperature line broadening due to exchange processes was observed, particularly in the ^{19}F spectrum. The three groups of phosphoranyl fluorine resonances had coalesced by 293 K, but the spectra had still not reached the high-temperature limit at 353 K, the highest temperature considered safe for sealed tubes containing these solvents. The study was then repeated using $CDCl_3$ as solvent, and it was found necessary to go to lower temperatures than were needed in the earlier experiments, in order to achieve the limiting spectra. The implication of this is that external factors, such as the nature of the solvent, do have some influence on the rate of the intramolecular rearrangements.

The PF_2 group fluorine resonances were sharp at 187 K, poorly resolved at 215 K, and had reached the high-temperature limit by 231 K. The PF_4 group phosphorus resonances were still well resolved at 218 K, but were broad at 298 K, and did not reach their high-temperature form until *ca.* 320 K. The PF_4 group fluorine resonances, with chemical shifts differing by up to 3 kHz, were sharp at 187 K, showing signs of broadening at 215 K, and between 240 and 290 K were a band some 5 kHz wide, barely distinguishable from the baseline. By 299 K a pair of broad resonances in the mean position could be observed, at 329 K further structure was resolved, and at 374 K, the highest temperature considered safe, the resonances were approaching the high-temperature limit, although the smallest couplings could still not be resolved.

The collapse of the three PF_4 fluorine sets of resonances into a single set, but with retention of couplings to other nuclei, indicates that an intramolecular rearrangement is taking place. There is no evidence for the axial fluorines exchanging with each other prior to the onset of axial–equatorial exchange, and it is therefore clear that rotation about the P–N bond cannot commence before pseudo-rotation. We attribute the resistance to both these processes to an interaction between the hydrogen atom and one of the axial fluorine atoms, which is possible if the molecule adopts the depicted conformation (Figure). Equivalent interactions have been proposed to account for similar resistance to rearrangement in other amino-fluorophosphoranes.[11,12]

The observed n.m.r. parameters are listed in Table 2: most of them are fully consistent with those reported for related compounds, in particular $NMe(H)(PF_4)$ [4] and $NMe(PF_2)(PF_4)$.[2] It has been noted [13,14] that $^1J(^{31}P-^{15}N)$ is positive for phosphorus(III) compounds, but in phosphorus(V) compounds the coupling is much smaller and may be negative. The two values recorded here are therefore probably of opposite sign, being +84.0 and −69.5 Hz for $J(P'N)$ and $J(PN)$ respectively. The value of $^2J(PP')$ (14.7 Hz) is much smaller than those recorded for amines with two phosphorus(III) substituents,[7,15,16] where there is the possibility of interaction between the two phosphorus lone pairs of electrons.

The couplings between the three types of fluorine nucleus of the PF_4 group and nuclei separated from them by two or more bonds are of particular interest. For the equatorial fluorine nuclei each of the four relevant couplings (to ^{15}N, ^1H, $^{31}P'$, and $^{19}F'$) is too small to be resolved. Of the two axial fluorine nuclei, the one labelled F_a couples more strongly than F_b to ^{15}N (11.5 and 3.9 Hz respectively), whereas F_b has the stronger coupling to ^1H (31.0 and 1.0 Hz), $^{31}P'$ (209.2 and 14.7 Hz), and $^{19}F'$ (14.7 and 0 Hz). We interpret these in terms of the presumed structure of the molecule (Figure), in which one axial fluorine atom lies close to the hydrogen atom, and the PF_2 group adopts a conformation which allows close contact between its two fluorine atoms and the proton, as observed in other aminofluorophosphines.[8,17,18] In this structure, the phosphorus lone pair of electrons is directed towards one of the axial fluorine atoms, and it may be expected that there should be very strong interaction between these two atoms. This might well give rise to the extraordinarily large coupling $^3J(^{31}P'-^{19}F_b)$, and to the large $^4J(^{19}F_b-^{19}F')$. It is interesting that the

fluorine nucleus with the largest three-bond coupling to phosphorus (presumed to be *cis*) also has the largest coupling to the proton, which must therefore be *trans*. However, the variation of ^3J(FCCH) in fluoroethanes has been studied,[19,20] and shows a maximum for a dihedral angle of 180°, with a smaller maximum at 0°, and minima at 90 and 270°. The observed set of values suggest that there is a similar relationship for ^3J(FPNH). We have interpreted couplings in several other molecules in terms of orientations of groups relative to a phosphorus lone pair. For example, in $PF_2[NH(GeH_3)]$,[16] in which the proton is probably *cis* to the lone pair, $^2J(^{31}P-^1H)$ is large (32.7 Hz); in $PF_2[NH(SiH_3)]$ and $PF_2(NH_2)$, which have N–H bonds approximately orthogonal to the phosphorus lone pairs, these couplings are *ca.* 18 Hz.[8,17,21] In the present case, the proton is probably *trans* to the lone pair, and $^2J(^{31}P'-^1H)$ is an order of magnitude smaller than usual.

The parameters involving the PF_4 group nuclei in the high-temperature spectra were close to the means of the values determined at low temperatures (Table 3). In

TABLE 3

Temperature dependence of n.m.r. parameters [a]

	Low temperature				High temperature
Parameter	F_a	F_b	F_c	Weighted mean	
$\delta(^{19}F)$/p.p.m.	−48.3	−41.8	−73.4	−59.2	−59.4
$^1J(^{31}P-^{19}F)$/Hz	801.7	766.5	965.5	874.8	875
$^2J(^{19}F-^{15}N)$/Hz	11.5	3.9	<0.2	7.7	n.r.
$^2J(^{31}P'-^{19}F)$/Hz	14.7	209.2	<0.2	56.0/48.6 [b]	49
$^3J(^{19}F-^1H)$/Hz	1.0	31.0	<0.2	8.0	n.s.
$^4J(^{19}F-^{19}F')$/Hz	<0.2	14.0	<0.2	3.5	4.9

[a] In CD_2Cl_2–$SiMe_4$ at 220 and 333 K; n.r. = not resolved, n.s. = not studied. [b] Depending on the relative signs of $J(P'F_a)$ and $J(P'F_b)$.

the case of $^3J(^{31}P'-^{19}F)$, however, the weighted mean value is 56.0 Hz, compared with an observed value of 49 Hz. This implies either that one or more of these couplings is highly temperature dependent, or that the values of the couplings to F_a and F_b are of opposite sign. If the latter is assumed, the mean coupling becomes 48.6 Hz, in excellent agreement with the observed value.

Vibrational Spectra.—Details of i.r. spectra of the gas and solid phases, and Raman spectra of the liquid phase, are given in Table 4. We have not attempted to make detailed assignments since the results for a molecule with nine atoms of comparable mass, and at best one element of symmetry, would be meaningless in the absence of a complete vibrational analysis, and a derived potential-energy distribution. It should be noted, however, that the spectrum includes bands in the regions associated with stretching and deformation vibrations of PF_4X and PF_2X groups. On ^{15}N substitution there are shifts of bands from 1 030 to 1 022, 911 to 903, and 784 to 775 cm^{-1}, which indicates that these modes include substantial contributions from the two P–N stretches.

Of particular importance are the N–H stretch and deformation modes. In the gas phase, only one band is seen in each of the regions associated with these vibr-

TABLE 4

Vibrational spectra (cm^{-1}) of $NH(PF_2)(PF_4)$

I.r. (gas)	I.r. (solid)	Raman (liquid)	Assignment
3 413m	3 353m	3 410s, br	ν(NH)
	3 303m	3 340mw	
1 328s	1 342s		δ(NH)
1 030vs	1 051s	1 005w	$\nu(PF_{cis})$
990vs	1 002s	993vw	ν(PN)
911s	909s	921w,br	
886vs	854s	885m,br	$\nu(P'F'_{cis})$
833vs		836s,br	
818 (sh)	819vs	810m,br	
784s	780vs	789s	ν(P'N)
	740 (sh)	755m	
	686m		$\nu(PF_{ax})$
614m	622vw	635m	$\delta(PF_{ax}N)$
565ms	558m	572w	
541m	539m		
515m	516m	518w	
	482w	494w	deformations and torsions
	469w	446w	
445m	442w	440w	
	427w	433w	
	418w	414w	
393m	397m	402m	
358w		359w	
350w	350w		
324vw	323w	333w,br	
295vw	301w		
274vw		276s	
		226m	
188w			
162w		155mw,br	

s = Strong, m = medium, w = weak, v = very, br = broad, and sh = shoulder.

ations, indicating that there is probably only one gas-phase conformer of this compound. In this respect it differs from $PF_2[NH(SiH_3)]$ [8] and $PF_2[NH(GeH_3)]$.[16] In the solid phase, the stretching mode is shifted to lower frequency and splits into two, while the deformation is shifted to slightly higher frequency. These changes suggest that hydrogen bonding is of greater significance in the solid than in the gas phase, presumably involving intermolecular contacts. We hope to be able to study these interactions by determining the structure of this compound in the crystalline phase.

Mass Spectra.—In Table 5 are listed the ions observed in mass spectra of $NH(PF_2)(PF_4)$, run with ionising voltages of 70 and 16 eV.* These data indicate that the parent ion can dissociate in several ways. At low ionising voltage the $[PF_3(NH)]^+$ ion gives the strongest peak in the spectrum, and at 70 eV a metastable ion peak is observed corresponding to the formation of this ion by elimination of PF_3 from the parent. This ready elimination of PF_3 is easily rationalised in terms of the proposed structure, in which the phosphorus atom of the PF_2 group lies close to one fluorine atom of the PF_4 group. The $[PF_3(NH)]^+$ ion subsequently eliminates NH.

The parent ion can also lose one or two fluorine atoms and a hydrogen atom, to give the ions $[NH(PF_2)(PF_3)]^+$, $[NH(PF_2)_2]^+$, and $[N(PF_2)(PF_3)]^+$, and peaks observed at *m/e* 134.3, 151.0, and 135.1 are assigned to the processes

* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

TABLE 5

Mass spectra of $NH(PF_2)(PF_4)$

m/e	Relative abundance at 70 eV	Relative abundance at 16 eV	Assignment
191	2	3	$[NH(PF_2)(PF_4)]^+$
172	13		$[NH(PF_2)(PF_3)]^+$
171	54	72	$[N(PF_2)(PF_3)]^+$
153		17	$[NH(PF_2)_2]^+$
152	43		$[N(PF_2)_2]^+$
107	79		$[PF_4]^+$
104	54	14	$?[PF_3(NH_2)]^+$, $[PF_2O]^+$
103	85	100	$[PF_3(NH)]^+$
88	18	11	$[PF_3]^+$
85	48		$?[PF_3(NH_2)]^+$, $[PF_2O]^+$
69	100		$[PF_2]^+$
66.5	5		$[N(PF)(PF_2)]^{2+}$
65	10	11	$[PF(NH)]^+$
46	14		$[P(NH)]^+$
44	1		$[PF_3]^{2+}$

Metastable ions

55.5w	$[NH(PF_2)(PF_4)]^+$	$\longrightarrow PF_3 + [PF_3(NH)]^+$
75.2w	$[PF_3(NH)]^+$	$\longrightarrow NH + [PF_3]^+$
115.6w	$[NH(PF_2)_2]^+$	$\longrightarrow HF + [N(PF)(PF_2)]^+$
134.3w	$[NH(PF_2)(PF_3)]^+$	$\longrightarrow HF + [N(PF_2)_2]^+$
135.1m	$[N(PF_2)(PF_3)]^+$	$\longrightarrow F + [N(PF_2)_2]^+$
151.0w	$[NH(PF_2)_2]^+$	$\longrightarrow H + [N(PF_2)_2]^+$

m = Medium and w = weak.

in which these ions lose HF, H, and F respectively, in each case giving $[N(PF_2)_2]^+$. Fairly strong peaks due to $[PF_4]^+$ suggest that cleavage of a P–N bond of the parent ion is also significant. Similar easy loss of one ligand from aminofluorophosphoranes has been noted several times.[3,4,12]

Photoelectron Spectrum.—He(I) u.v. photoelectron spectra were recorded for $NH(PF_2)(PF_4)$ and for $PF_2(NPF_3)$, and details are given in Table 6, with assignments made by comparison with observed ionisation potentials for other compounds.[7,12,22] For each of the compounds studied, the phosphorus lone-pair ionisation potential is greater than in other related aminofluorophosphines, and the nitrogen lone-pair ionisation potential is similarly large, particularly for $NH(PF_2)(PF_4)$. This may simply reflect the electron-withdrawing properties of the groups with three or four fluorine atoms. In the case of $PF_2(NPF_3)$, the nitrogen lone-pair level will be mixed to some extent, depending on the P–N–P angle, with the P=N π-bonding level. The latter has not been assigned, but may give rise to part of the band at 12.6 eV.

TABLE 6

He(I) u.v. photoelectron spectra

Ionisation potential (eV) $NH(PF_2)(PF_4)$	Ionisation potential (eV) $PF_2(NPF_3)$	Assignment
11.6	11.2	N 2*p*
12.7	12.6	P 3*p*, ? P–N π
15.6	16.3	P–N σ, N–H σ
16.2, 17.4	17.6	F 2*p* π
17.8	18.0	P–F σ
18.6	18.6	P–F σ

EXPERIMENTAL

All volatile compounds were handled using a Pyrex glass vacuum line, fitted with Sovirel greaseless taps. Difluoro(silylamino)phosphine was prepared from aminodifluorophosphine and bromosilane,[8] and phosphorus pentafluoride was obtained by heating a diazonium hexafluorophosphate *in vacuo*.

N.m.r. spectra were recorded on Varian Associates XL100 and HA100 spectrometers, the latter modified to accept a second frequency, derived from a Schlumberger FS30 frequency synthesizer. Vibrational spectra were obtained using Perkin-Elmer 225 and 557 and Beckmann-RIIC FS270 i.r. spectrometers, covering the ranges 200—4 000 and 50—400 cm^{-1} respectively, and a Cary 82 Raman spectrometer, with 647.1-nm Kr laser excitation. For mass spectra, an A.E.I. MS902 spectrometer was used, and for photoelectron spectra, a Perkin-Elmer PS16 spectrometer, with He(I) (21.22 eV) excitation.

Preparation of Difluorophosphino(tetrafluorophosphoranyl)amine.—A glass ampoule (40 cm^3) fitted with a greaseless tap was dried by allowing gaseous bromosilane to stand in it for a few minutes. Then $PF_2[NH(SiH_3)]$ (1.00 mmol) and PF_5 (1.10 mmol) were condensed into the ampoule, and allowed to warm to room temperature for 15 s. The products were separated by fractional condensation *in vacuo*. The major products were fluorosilane (1.00 mmol) and *difluorophosphino(tetrafluorophosphoranyl)amine* (0.93 mmol, 93%, almost involatile at 195 K), with small amounts of $PF_2(NPF_3)$, PF_3, and a white solid.

Reaction of $PF_2(NH_2)$ *with* PF_5.—Phosphorus pentafluoride (0.2 mmol) and $PF_2(NH_2)$ (0.3 mmol) were warmed together to room temperature in a glass ampoule. A white solid was formed, and the only volatile material recovered was unchanged $PF_2(NH_2)$ (0.1 mmol).

Reactions between $NH(PF_2)(PF_4)$ *and* HX (X = Cl *or* Br).—In a typical experiment, $NH(PF_2)(PF_4)$ (0.3 mmol) and HCl (0.9 mmol) were allowed to mix in an n.m.r. tube, with C_6D_6 as solvent. After *ca.* 10 min at room temperature, white solids were seen to be slowly forming. N.m.r. spectra showed unchanged amine to be present, with only a trace amount of $PClF_2$.

Attempted Preparations of $NH(PF_2)(PF_2O)$ *and* $NH(PF_2)(PF_2S)$.—Equimolar amounts of $PF_2[NH(SiH_3)]$ and PF_3O, PF_3S, $PClF_2S$, or $PF_2I(S)$ were condensed into an n.m.r. tube, with a mixture of $CDCl_3$ and $SiMe_4$ as solvent. The reaction mixture was monitored by ^{19}F or ^{31}P n.m.r. spectroscopy as it was warmed to room temperature or above. In no case was any reaction observed, other than the slow decomposition of the starting amine by elimination of $SiFH_3$.

We thank Dr. S. Cradock for assistance in obtaining and interpreting photoelectron spectra, Dr. A. P. Lane and Mrs. L. Evans, Glasgow University, for the provision of facilities and for obtaining Raman spectra, and the S.R.C. for the award of a research studentship (to J. G. W.).

[8/1445 *Received*, 4*th August*, 1978]

REFERENCES

[1] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 1969, **8**, 2436.
[2] J. S. Harman, M. E. McCartney, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1971, 1547.
[3] A. H. Cowley and J. R. Schweiger, *J.C.S. Chem. Comm.*, 1972, 560.
[4] M. Lustig and H. W. Roesky, *Inorg. Chem.*, 1970, **9**, 1289.
[5] J. S. Harman and D. W. A. Sharp, *Inorg. Chem.*, 1971, **10**, 1538.
[6] D. E. J. Arnold, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1976, 823.

[7] D. E. J. Arnold and D. W. H. Rankin, *J.C.S. Dalton*, 1975, 889.
[8] D. E. J. Arnold, E. A. V. Ebsworth, H. F. Jessep, and D. W. H. Rankin, *J.C.S. Dalton*, 1972, 1681.
[9] R. Schmutzler, *Angew. Chem. Internat. Edn.*, 1964, **3**, 753.
[10] S. C. Peake and R. Schmutzler, *J. Chem. Soc.* (*A*), 1970, 1049.
[11] E. L. Muetterties, P. Meakin, and R. Hoffman, *J. Amer. Chem. Soc.*, 1972, **94**, 5674.
[12] D. E. J. Arnold and D. W. H. Rankin, *J.C.S. Dalton*, 1976, 1130.
[13] J. R. Schweiger, A. H. Cowley, E. A. Cohen, P. A. Kroon, and S. L. Manatt, *J. Amer. Chem. Soc.*, 1974, **96**, 7122.
[14] D. W. W. Anderson, J. E. Bentham, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 1215.
[15] J. F. Nixon, *J. Chem. Soc.* (*A*), 1969, 1087.
[16] E. A. V. Ebsworth, D. W. H. Rankin, and J. G. Wright, *J.C.S. Dalton*, 1977, 2348.
[17] G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc.* (*A*), 1971, 785.
[18] M. Barrow, E. A. V. Ebsworth, M. M. Harding, and S. G. D. Henderson, *J.C.S. Dalton*, in the press.
[19] K. Hirao, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, 1973, **95**, 31.
[20] K. L. Williamson, Y.-F. Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, 1968, **90**, 6717.
[21] D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1971, 783.
[22] S. Cradock and D. W. H. Rankin, *J.C.S. Faraday II*, 1972, 940.

Proofs to: Professor E.A.V. Ebsworth
Department of Chemistry
University of Edinburgh
West Mains Road
Edinburgh EH9 3JJ

Derivatives of acetamide containing PF_2- groups.

by E.A.V. Ebsworth, D.W.H. Rankin, W. Steger and (in part) J.G. Wright.

Bis(trimethylsilyl) acetamide reacts with an equimolar proportion of PF_2Br at -80°C to give $CH_3C(OSiMe_3):NPF_2$. With an excess of PF_2Br, the initial product at -80°C is $CH_3C(OPF_2):NPF_2$; at temperatures above -40° there is a slow rearrangement to give a mixture of $CH_3C(OPF_2):NPF_2$ and $CH_3CO[N(PF_2)_2]$ All these PF_2- derivatives of acetamide decompose slowly at room temperature to give acetronitile and either PF_2OSiMe_3 or $(PF_2)_2O$. They have been characterised by ^1H, ^{19}F and ^{31}P nmr and by infrared spectroscopy. There was no evidence for fast exchange of PF_2- groups between N- and O- sites.

Bis(trimethylsilyl)acetamide, (I), has proved to be an important silylating agent.[1] The nmr and infrared spectra indicate that the compound should not be described as an amide, but rather as an oxyimine, with one trimethylsilyl group bound to nitrogen and one to oxygen.[2] There is exchange of trimethylsilyl groups between the two sites that is rapid on the ^{1}H-nmr timescale at room temperature but at low temperature is slow enough to allow observation of two separate resonances in the Me_3Si- region.[2] In the past we have synthesised a range of new compounds containing PF_2- groups by exchanging between PF_2Br and silyl, germyl and stannyl derivatives,[3,4] and as part of this programme we have investigated the reaction between PF_2Br and (I). We hoped that the use of ^{31}P and ^{19}F nmr spectroscopy would enable us to characterise any products relatively easily, and would also afford a way of investigating any possible exchange processes over a range of possible timescales.

Results

The ^{31}P and ^{19}F nmr spectra of a solution containing equimolar proportions of PF_2Br and (I) at -80° showed that all the PF_2Br initially added was rapidly consumed, the ^{1}H-nmr spectrum established that Me_3SiBr was liberated. Only one ^{31}P resonance was observed from the products: this showed the wide triplet coupling associated with a PF_2- group. The proton resonance spectrum of the purified reaction product shows two sharp singlets with the relative intensities 1:3. These spectra are most easily explained if we suppose that one trimethylsilyl group has been exchanged for PF_2, giving a

product containing one PF_2- group and one trimethylsilyl group bound to the amide function:

$$CH_3C(O,N)(SiMe_3)_2 + PF_2Br = CH_3C(O,N)(SiMe_3)(PF_2) + Me_3SiBr$$

The ^{31}P chemical shift of the product (see Table 1) is consistent with P bound to N rather than O, and varies with temperature as found in relative derivatives known to contain PF_2N- groups;[4] furthermore, the lines in the ^{31}P spectrum are somewhat broadened, presumably as a result of interaction with the quadrupole moment of ^{14}N. This broadening is often observed in PF_2N- compounds,[4] but not in derivatives containing PF_2- bound to[5] O. The line-widths increased slightly when the temperature was reduced, and this line did not split, so we do not believe that the broadening is due to an exchange process. We therefore conclude that PF_2- is bound to N in our product. The infrared spectrum (see Table 2) shows no strong band in the region associated with C=O groups, but a weak band at 1590 cm^{-1} which can be associated with a C=N- unit in the molecule, and so we formulate (II) as $CH_3C(OSiMe_3):NPF_2$.

The nmr spectra of (II) show no evidence of exchange involving PF_2- groups such as additional line-broadening at temperatures up to 30°. However, at room temperature the compound decomposes over a period of hours, forming Me_3SiOPF_2 and CH_3CN.

If a three-fold molar excess of PF_2Br was taken initially, the ^1H resonance spectrum of the product at -80° showed that the only compound present containing the Me_3Si- group was Me_3SiBr. It is evidence that both Me_3Si- groups were eliminated from (I) by exchange:

$$CH_3C(O,N)(SiMe_3)_2 + 2\ PF_2Br = CH_3C(O,N)(PF_2)_2 + 2\ Me_3SiBr$$

Two different triplet resonances were observed in the ^{31}P spectrum at -80^{o}; the large triplet couplings showed that both were due to PF_2- groups. One set of triplet lines were substantially broader than the other, and its chemical shift correspond to that expected from PF_2N- compounds: the other triplet was sharper, and the associated chemical shift was in keeping with that expected from a PF_2- group bound to O. We conclude that the initial product of the reaction, (IIIa), contains one PF_2- group bound to N and the other bound to O:

$CH_3C(OPF_2):NPF_2$ (IIIa).

In keeping with this conclusion, the ^{19}F spectrum showed two doublets, the splittings corresponding to those in the two triplets from the ^{31}P spectrum. There were no significant changes in the ^{31}P or the ^{19}F spectra as the sample was allowed to warm from -80^{o} to -40^{o}; none of the lines broadened, though the chemical shift of the PF_2N- phosphorus nucleus changed somewhat. At -20^{o}, new peaks began to appear in both ^{31}P and ^{19}F spectra, and after half an hour at room temperature the nmr spectra indicated that there was about three times as much of the new material as of (IIIa). The new species showed a single set of PF_2- resonances in both ^{31}P and ^{19}F spectra. The peaks were somewhat broadened, particularly in the ^{31}P spectrum. Second-order effects could clearly be distinguished, implying that at least two PF_2- groups were bound to the same heteroatom; the spectra clearly resembled those obtained from $(PF_2)_2NH$, and could be analysed approximately on the assumption that the spin-system was of the form $(AX_2)_2Q$.

These observations, together with the ^{31}P chemical shift (in the region characteristic of PF_2N) show that the new species is an isomer of (IIIa) in which both PF_2- groups are bound to nitrogen:

$CH_3CON(PF_2)_2$ (IIIb).

The ^1H resonance spectrum of the pure mixture (IIIa/111b) at room temperature does not give much information but shows a complicated line pattern due to very small and slightly different coupling constants of the two isomers which have almost identical chemical shift values as well. When the solution was cooled again to -50° and kept at that temperature for some time, the relative intensities of peaks due to (IIIa) and (IIIb) remained unchanged; there was no evidence of exchange between the two forms at any temperature we studied. The molar proportions of (IIIa) and (IIIb) did not change if the solution was left at room temperature for a long time; slow decomposition led to the formation of $(PF_2)_2O$ and CH_3CN. The nmr parameters are given in Table 1.

It proved possible by low temperature fractionation to obtain samples of (II) and of (IIIa/b) whose infrared spectra were free of peaks dur to Me_3SiBr. The spectra help to confirm that the structures we propose are correct. The spectrum of (II) contains peaks due to Me_3Si- groups, but no strong band that can be assigned to ν (CO); the spectrum of (IIIa/b) contains a band in the region associated with ν (CO), but no strong bands assignable to Me_3Si groups. The observed frequencies, with tentative assignments, are given in Table 2.

We have also recorded the mass spectrum of the equilibrium mixture of (IIIa/b). We were able to detect a weak peak due to the molecular ion, together with peaks due to CH_3CN^+, $(PF_2)_2O^+$ and PF_2O^+.

Treatment of (IIIa/b) with water gave a white solid whose ^1H, ^{19}F and ^{31}P nmr spectra led us to identify it as $CH_3CONHPF_2$ (IV) which was also formed in traces when PF_2Br reacted with CH_3CONH_2. It too decomposed slowly at room temperature. Reaction between acetamide and PF_2Br led to the formation of traces of (IV), together with large quantities of white solid; however, no derivatives of acetamide containing PF_2- groups could be detected among the products of reaction between PF_2NH_2 and acetyl chloride. There was no reaction between PF_2Br and bis(trimethylsilyl) trifluoroacetamide at temperatures up to $+80^o$.

Discussion

It is clear from these results that although amide-type derivatives in which PF_2- groups are bound to the amide function can be obtained, they do not show exchange of PF_2 groups between O- and N- sites that is fast on the nmr time-scale at room temperature, as would be analogous to the exchange of Me_3Si- groups between O and N sites in the silyl amides. The initial exchange between (I) and PF_2Br involves the trimethylsilyl group that is bound to N. At least with respect to PF_2Br the two trimethylsilyl groups show quite different reactivities and there is no evidence that in (II) the remaining trimethylsilyl group spends any of its time bound to N rather than O. If fast exchange of Me_3Si between O and N does occur in (II) under the conditions of our experiments, either it must be so fast that even at -80^o the spectrum

observed is of the time-averaged environment, or the equilibrium must lie very heavily on the side of the form with Me_3Si- bound to O. The slow transformation of (IIIa) into a mixture of (IIIa) and (IIIb) indicates that some kind of isomerisation between (IIIa) and (IIIb) occurs that is slow at or just below room temperature, and the constancy of the composition of the mixture of (IIIa) and (IIIb) over a period of time implies that some sort of equilibrium is reached. We obtained no evidence for fast exchange of PF_2- groups between O and N sites in (III). Despite the initial formation of PF_2N- rather than PF_2O- species, the decomposition-products contain PF_2O- rather than PF_2N- bonds; this presumably reflects the thermodynamic stability of the other decomposition-product, acetonitrile. The thermal instability of all PF_2- amides is noteworthy.

The absence of any reaction between PF_2Br and $CF_3C(O,N)(SiMe_3)_2$ may well be associated with the electron-withdrawing properties of the CF_3- group, and implies that exchange of PF_2 for Me_3Si is associated with electrophilic attack at the amide function.

Experimental

Volatile compounds were handled in standard vacuum apparatus, fitted with greased glass or greaseless polyfluoroethylene (Sovirel) taps; involatile compounds that were sensitive to air or moisture were recorded by means of a Varian Associates EM 390 spectrometer, and ^{19}F and ^{31}P spectra were obtained by

means of a Varian Associates XL 100 spectrometer operating in the FT mode. (I) was obtained commercially and PF_2Br was prepared by an established method.

Reactions in nmr tubes. (I) (0.4 mmol) was introduced into an nmr tube in the glove-box; solvent (20% C_6D_6 and 80% toluene) was distilled into the tube on the vacuum-line, followed by the appropriate amount of PF_2Br. The tube was kept at 77K until the spectrum was to be recorded, when the sample was allowed to warm to the desired temperature in the nmr probe.

Preparation of (II). In a typical experiment, (I) (3.0 mmol) and PF_2Br (3.0 mmol) were allowed to mix in an ampoule fitted with a greaseless tap at room temperature (30 min). Repeated fractional distillation and condensation in the vacuum system gave a sample of (II) whose ^1H resonance and infrared spectrum showed the absence of Me_3SiBr and whose ^{19}F and ^{31}P spectra corresponded with those obtained from a similar reaction that was allowed to occur in toluene in an nmr tube. (II) was not very volatile in vacuum (vp = 20 mm at 293K); over a period of hours at room temperature it decomposed to CH_3CN and Me_3SiOPF_2 (both identified spectroscopically).[6]

Preparation of (III). (I) (5.0 mmol) and PF_2Br (15.0 mmol) were allowed to react at room temperature in an ampoule fitted with a greaseless tap. Repeated fractional distillation and condensation in the vacuum system gave a sample of (IIIa/b) whose infrared spectrum contained no peaks characteristic of

Me_3Si- groups. The infrared and raman spectra of this sample were recorded; the nmr spectra corresponded with those obtained from the product of a similar reaction in an nmr tube. On standing for several hours at room temperature, the compound decomposed slowly into CH_3CN and $(PF_2)_2O$ (both identified spectroscopically).[5]

Reaction of (III) with water. (III) (4.0 mmol) and H_2O (2.0 mmol) were allowed to react together in an ampoule to whose side was sealed an nmr tube. A white solid soon formed at room temperature. Volatile materials were removed, $CDCl_3$ and Me_4Si were distilled into the tube and the solution sealed in the nmr tube. The spectra established that the product was $CH_3CONHPF_2$; the nmr parameters are given in Table 1.

Reaction of PF_2Br with CH_3CONH_2. Dried acetamide (0.8 mmol) was allowed to react with PF_2BR (0.4 mmol) at room temperature in $CDCl_3$. A substantial amount of white fluffy solid was formed immediately. The nmr spectrum of the product showed that a small amount of $CH_3CONHPF_2$ had been formed.

Reaction of PF_2NH_2 with CH_3COCl. When PF_2NH_2 (1.50 mmol) was allowed to react with CH_3COCl (1.00 mmol) at room temperature. White and pale yellow solids were formed. The only volatile material recovered was PF_3 (0.4 mmol) and a mixture of PF_2NH_2 and CH_3COCl (0.9 mmol in all). When PF_2NH_2 (1.00 mmol), CH_3COCl (1.10 mmol) and Me_3N (1.00 mmol) were allowed to react together, the volatile material recovered was a mixture of PF_2NH_2 and CH_3COCl (0.65 mmol).

Reaction of $CF_3CON(SiMe_3)_2$ with PF_2Br. Mixing these two reagents in varying concentration-roughly at temperatures of up to 323K led only to the recovery of starting-materials.

We are grateful to NATO for a scholarship to one of us, W.S.

TABLE 1. Nmr parameters for PF_2 derivatives of acetamide.

Compound	δ(P), ppm		δ(F), ppm	δ(CH_3C), ppm	^1J(PF), Hz
	213K	273K	273K	273K	273K
II	158.5	155.2	-63.8	1.86[a]	1248
IIIa: OPF_2	121.2	121.4	-56.3	*2.33*	1340
NPF_2	151.7	148.5	-65.7		1269
IIIb	145.3	146.0[b]	-69.4	*2.39*	1297
IV	nm	144.1[c]	-72.8	*2.15*	1235

[a] δ(H)(Me_3Si) = 0.31 ppm.

[b] δ ^2J(PP) = *32.7*; ^3J(PF) = +34.9; ^4J(PH) = *4.5*; ^5J(FH) = *0.9* Hz

[c] (NH) = 7.0 ppm; ^3J(FH) = *4.2*; ^4J(PH) = *2.4*; ^5J(FH) = *0.4* Hz.

nm means not measured. Italic values were obtained from solutions in $CDCl_3$; others from solutions in C_6D_6/C_7H_8.

TABLE 2. Infrared spectra of PF_2- derivatives of acetamide.

Frequencies (cm^{-1})			Assignments[7]
II	IIIa/b mixture		
vapour	vapour	liquid film	
2975 m	2980 w	2980 w	νCH
2920 w			
1700 w br		1704 w br	?2x855
	1660 vw	1655 mw	νCO
1590 w		1605 w	νC=N
1425 w			δCH_3(asym)
1270 s			δCH_3Si(sym)
		1259 mw	
1120 w			
	1080 m	1090 mw	νPOC
		1045 mw	
1042 vs			νSiOC
	980 vs	980 vs	νPNC
862 vs	855 vs br	855 vs br	νPF and (?)ρCH_3Si
815 s			
	680 m	680 ms	
518 mw	520 m	521 m	δPF_2
		468 mw	

v = very; br = broad; s = strong; m = medium intensity; w = weak.

References

1. L. Birkhofer and A. Ritter, Angew. Chem., 77, 414 (1965).

2. W. Kantlehner, W. Kugel and A. Bredereck, Chem. Ber., 105, 2264 (1972).

3. E.A.V. Ebsworth, D.J. Hutchison and D.W.H. Rankin, to be published.

4. D.E.J. Arnold, E.A.V. Ebsworth, H.F. Jessep and D.W.H. Rankin, J.C.S. Dalton, 1972, 1681.

5. J.F. Nixon, "Adv. Inorg. Chem", Radiochem, (ed. Emeleus and Sharpe), Wiley, 1970, 13, p. 363.

6. R.G. Cavell, R.D. Leary, A.R. Sanger and A.J. Tomlinson, Inorg. Chem., 12, 1374 (1973).

7. D.E.C. Corbridge, "Topics in Phosphorus Chemistry", Interscience, New York, 1971, vol. 6, p.235.

Proofs to: Dr D.W.H. Rankin
Department of Chemistry
University of Edinburgh
West Mains Road
Edinburgh EH9 3JJ

Journal of the Chemical Society, Dalton Transactions

Preparation and N.m.r. Spectra of Aminodifluorophosphorane

By D.W.H. Rankin* and J.G. Wright†
Department of Chemistry, University of Edinburgh, West Mains Road,
Edinburgh EH9 3JJ

Aminodifluorophosphine has been prepared by the reaction in solution of difluorophosphine and ammonia. N.m.r. spectra indicate that the fluorine atoms are in axial positions and that the amino group atoms lie in a plane perpendicular to the equatorial plane. At 215 K there is no evidence for rotation about the P-N bond or for fluxional behaviour. The compound is thermally unstable, and has not been isolated.

---

† Present address: Department of Chemistry, City of London Polytechnic, Jewry Street, London ~~EC4~~ EC3N 2EY.

The oxidative addition of primary amines to substituted difluorophosphines has been used as a means of preparing phosphoranes which have P-H bonds[1], and it has also been shown[2] that ammonia may act as the formal oxidising species in the preparation of diaminodifluorophosphorane. There have been no reports of such oxidative addition reactions with unsubstituted difluorophosphine to give difluorodihydrophosphoranes. There is, however, a report of the addition of alcohols and alkyl thiols to difluorophosphine, giving dihydrophosphoranes[3]: the products were reported to be very unstable. The only other known phosphoranes with more than one P-H bond are PF_3H_2 and PF_2H_3, and there is a marked decrease in the stability of the fluorophosphoranes as the number of hydrogen atoms increases[4,5].

We have now studied the oxidative addition of ammonia to difluorophosphine to give aminodifluorophosphorane. This is a simple compound which may be expected to have a high degree of symmetry, and to be suitable for detailed spectroscopic analysis. Its stability, however, is such that we have been unable to isolate it, and we report here the results of a limited study of its n.m.r. spectra, recorded at low temperatures.

Results and Discussion

When ammonia and difluorophosphine were allowed to mix in solution a rapid reaction took place. Large amounts of an orange-red solid were formed, and further precipitation of solid occurred subsequently, even while spectra were being recorded at 215 K. N.m.r. spectra of the solution indicated that a simple addition reaction was occurring, followed by decomposition, which gave trifluorophosphine as the only soluble product.

$$PF_2H + NH_3 \rightarrow PF_2H_2(NH_2)$$

$$\rightarrow PF_3 + \text{insoluble solids.}$$

The product of the reaction was unequivocally identified by the ^{1}H, ^{19}F and ^{31}P n.m.r. spectra of samples made using $^{15}NH_3$. The ^{31}P spectrum was first order, and consisted of a triplet (754 Hz) of triplets (599 Hz) of doublets (41 Hz) of triplets (13 Hz). The first and last of these splittings were removed by ^{1}H noise decoupling. The ^{1}H spectrum had two groups of resonances, of equal area. The higher frequency group, assigned to the hydrogen atoms bound to phosphorus, showed first order couplings to ^{31}P, ^{19}F and ^{15}N, giving a total of 12 lines, but long range HH coupling was not resolved. The other group of proton resonances, and the ^{19}F spectrum, each showed two or three first order splittings, giving sets of identical second order subspectra. These were not completely resolved, but nevertheless indicated that the fluorine and amino hydrogen atoms formed an $[AX]_2$ spin sub-system, and analysis of the spectra gave values for the two different FH couplings, and upper limits for the FF and HH couplings.

The n.m.r. parameters are listed in the table. The ^{1}H and ^{31}P chemical shifts and the large $^{1}J(^{31}P^{1}H)$ are all consistent with the phosphorane formulation[2,4,6]. The one-bond P-F coupling is amongst the smallest reported, and indicates that the fluorine atoms occupy the axial positions of the trigonal bipyramidal structure[7], while the large value for $^{1}J(^{15}N^{1}H)$ implies a large s orbital contribution to the N-H bonds[8], and hence that the PNH_2 group is probably planar. Finally, the magnetic non-equivalence of the amino protons and of the fluorine atoms, combined with the magnetic equivalence of the phosphorane protons, implies that the plane of the amino group is aligned perpendicular to the equatorial plane, giving the molecule overall C_{2v} symmetry, and that at 215 K there is restricted rotation about the P-N bond. Thus the behaviour of the amino group with respect to rotation in this compound parallels that found for other aminofluorophosphoranes[2,9].

Experimental

Volatile materials were handled using a conventional pyrex glass vacuum line fitted with greaseless taps. Difluorophosphine was prepared by the reaction of difluoroiodophosphine, phosphine and mercury.

N.m.r. tube preparation of $PF_2H_2(NH_2)$ - Typically, [^{15}N]-ammonia (0.5 mmol) was thoroughly mixed with CCl_3D and a trace of $SiMe_4$ in an n.m.r. tube. Difluorophosphine (0.5 mmol) was then condensed into the tube, which was then sealed. The solution was then warmed briefly to 270 K, with the formation of substantial amounts of orange-red solid. Spectra were recorded at 215 K, but decomposition continued at this temperature, and several samples were required for a complete set of spectra to be obtained. Spectra were recorded using Varian Associates XL100 and HA100 spectrometers.

Attempted isolation of $PF_2H_2(NH_2)$ - Ammonia (0.5 mmol) and PF_2H (0.5 mmol) were condensed together in a glass ampoule and warmed rapidly. On melting, they formed a yellow solid, which became orange and then brown. After one minute the volatile materials present were fractionated, but PF_3 (0.3 mmole) was the only product isolated.

Acknowledgement

We thank the Science Research Council for the award of a Research Studentship to J.G. Wright.

References

1. G.I. Drozd, S.Z. Ivin, V.V. Sheluchenko and M.A. Landau, Zh. Obshch. Khim., 1968, 38, 1653;

G.I. Drozd, S.Z. Ivin, V.V. Sheluchenko and B.I. Tetel'baum, Zh. Obshch. Khim., 1967, 37, 957.

2. D.E.J. Arnold and D.W.H. Rankin, J.C.S. Dalton, 1976, 1130.

3. L.F. Centofanti and R.W. Parry, Inorg. Chem., 1973, 12, 1456.

4. P.M. Treichel, R.A. Goodrich and S.B. Pierce, J. Amer. Chem. Soc., 1967, 89, 2017.

5. V.F. Seel and K. Velleman, Z. anorg. allgem. Chem., 1971, 385, 123.

6. J.S. Harman and D.W.A. Sharp, J. Chem. Soc. (A), 1970, 1935.

7. R. Schmutzler, Angew. Chem. Int. Ed., 1965, 4, 496;

J. Grosse and R. Schmutzler, Phosphorus, 1974, 4, 49.

8. G. Binsch, J.B. Lambert, B.W. Roberts and J.D. Roberts, J. Amer. Chem. Soc., 1964, 86, 5564.

9. E.L. Muetterties, R. Meakin and R. Hoffman, J. Amer. Chem. Soc., 1972, 94, 5674.

Table

N.m.r. parameters[a] for $PF_2H_2(^{15}NH'_2)$

$\delta(^1H)$	+6.90 ppm
$\delta(^1H')$	+2.05 ppm
$\delta(^{19}F)$	-57.5 ppm rel. to CCl_3F
$\delta(^{31}P)$	-57.3 ppm rel. to 85% H_3PO_4
$^1J(^{31}P^1H)$	754.4 Hz
$^1J(^{31}P^{19}F)$	598.6 Hz
$^1J(^{15}N^1H')$	88 Hz
$^1J(^{31}P^{15}N)$	41.1 Hz
$^2J(^{19}F^1H)$	89.6 Hz
$^2J(^{19}F^{15}N)$	13.2 Hz
$^2J(^{15}N^1H)$	4.7 Hz
$^2J(^{31}P^1H')$	13.0 Hz
$^2J(^1H'^1H')$[b]	< 1 Hz
$^2J(^{19}F^{19}F)$[b]	< 1 Hz
$^3J(^{19}F^1H')$[b]	17.2 Hz
$^3J(^{19}F^1H')$[b]	21.5 Hz
$^3J(^1H^1H')$	< 0.5 Hz

Notes: a Recorded at 215 K in 95:5 CCl_3D:$SiMe_4$.

b Derived by analysis of incompletely resolved $[AX]_2$ sub-spectra.